

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE TRANSMITTAL LETTER TO THE UNITED STATES^(a)	ATTORNEY DOCKET NO. 7398/72632
DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 USC 371	U S APPLICATION NO. (New Application) 10/070616
INTERNATIONAL APPLICATION NO. PCT/JP00/06093	INTERNATIONAL FILING DATE PRIORITY DATE CLAIMED September 7, 2000

TITLE OF INVENTION
Plastic Optical Fiber, Optical Fiber Cable, Plugged Optical Fiber Cable, and
Production Methods Thereof

APPLICANT(S) FOR DO/EO/US
FUKUBA et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 USC 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 USC 371.
 3. ☒ This is an express request to begin national examination procedures (35 USC 371(f)).
 4. ☐ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
 5. ☒ A copy of the International Application as filed (35 USC 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☐ An English language translation of the International Application as filed (35 USC 371(c)(2)).
 7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 USC 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
 8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 USC 371(c)(3)).
 9. ☐ An oath or declaration of the inventor(s) (35 USC 371(c)(4)).
 10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 USC 371(c)(5)).
 11. Nucleotide and/or Amino Acid Sequence Submission
 - a. ☐ Computer Readable Form (CRF)
 - b. Specification Sequence Listing on:
 - i. ☐ CD-ROM or CD-R (2 copies); or
 - ii. ☐ Paper Copy
 - c. ☐ Statement verifying identity of above copies
- Items 12 to 19 below concern other document(s) or information included:**
12. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 - ☐ Form PTO-1449
 - ☐ Copies of Listed Documents
 13. ☐ An assignment for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 14. ☒ A **FIRST** preliminary amendment.
 - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 15. ☐ A substitute specification.
 16. ☐ A change of power of attorney and/or address letter.
 17. ☒ Application Data Sheet Under 37 CFR 1.76
 18. ☒ Return Receipt Postcard
 19. ☒ Other items or information: Form PCT/IB/304, PCT/IB/308, International Search Report; IPER in Japanese

U.S. APPLICATION NO (New Application) 10/070616		INTERNATIONAL APPLICATION NO PCT/JP00/06093		ATTORNEY DOCKET NO 7398/72632	
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20. ■ The following fees are submitted:				CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$ 890.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO, but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$ 740.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$ 710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1) to (4) \$ 100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT=				\$890.00	
Surcharge of \$130.00 for furnishing the National fee or oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	40 - 20 =	20	x \$ 18.00	\$360.00	
Independent Claims	5 - 3 =	2	x \$ 84.00	\$168.00	
■ Multiple Dependent Claim(s) (if applicable)			+\$280.00	\$280.00	
TOTAL OF ABOVE CALCULATIONS=				\$1,698.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
SUBTOTAL=				\$	
Processing fee of \$130.00 for furnishing English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date.				\$	
TOTAL NATIONAL FEE=				\$1,698.00	
Fee for recording the enclosed assignment. The assignment must be accompanied by an appropriate cover sheet. \$40.00 per property				\$	
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a. ☐ A check in the amount of \$ to cover the above fee is enclosed.

b. ■ Please charge Deposit Account No. 06-1135 in the amount of \$1,698.00, under Order No. 7398/72632, to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ■ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 06-1135. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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March 8, 2002

 Date

PATENT

Attorney Docket No. 7398/72632

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

FUKURA et al.

Application No.: (New Application)

Filed: Herewith

For: Plastic Optical Fiber, Optical Fiber Cable, Plugged Optical Fiber Cable
and Production Methods Thereof

March 8, 2002

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Please enter this Preliminary Amendment:

IN THE SPECIFICATION:

Page 1, after the title, insert

Cross-Referenced Applications

This application is the National phase of International Application No. PCT/JP00/06093, filed September 7, 2000, which designated the U.S. and that International Application was not published under PCT Article 21(2) in English.

IN THE CLAIMS:

Please amend claims 10 and 21 as follows:

10. (Amended) A production method of a plastic optical fiber, comprising the step of annealing a plastic optical fiber obtained by heat-drawing an undrawn fiber obtained by melt

spinning, at a circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of 0.5 to 1.2 under heating conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$ wherein T_{gc} represents a glass transition temperature of a core, x represents an annealing temperature ($^{\circ}\text{C}$), and y : an annealing time (seconds).

21. (Amended) A production method of a plastic optical fiber, comprising the step of annealing a plastic optical fiber obtained by heat-drawing an undrawn fiber obtained by melt spinning, at a circumferential velocity ratio between (circumferential velocity of a rear roller / circumferential velocity of a front roller) between the front and rear rollers of 0.5 to 1.2 under heat conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$, wherein T_{gc} represents a glass transition temperature of a core, x represents an annealing temperature ($^{\circ}\text{C}$), and y represents an annealing time (seconds), while a tension of 0.35×10^6 to 1.5×10^6 Pa is applied to the fiber.

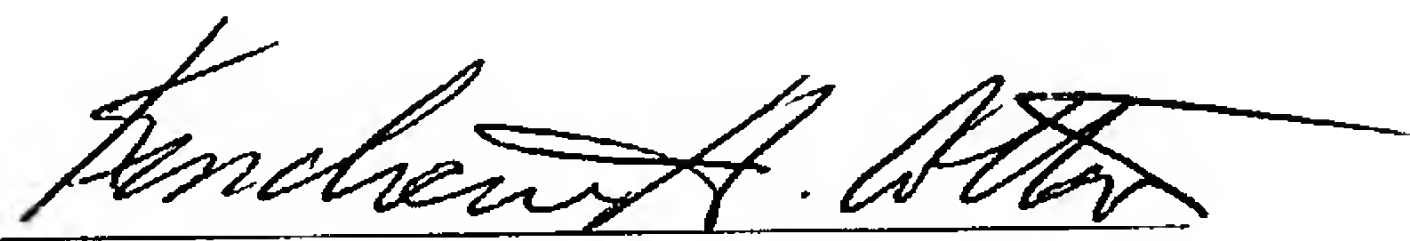
See the Appendix for amendments.

REMARKS

The First Amendment incorporates the application lineage per 35 U.S.C. § 120 and makes editorial corrections to claims 10 and 21 to place them in more conventional U.S. claim format.

Respectfully submitted,

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APPENDIX

Amendments to the existing claims:

10. (Amended) A production method of a plastic optical fiber, comprising the step of annealing a plastic optical fiber obtained by heat-drawing an undrawn fiber obtained by melt spinning, at a circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of 0.5 to 1.2 under heating conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$, wherein { T_{gc} : represents a glass transition temperature of a core, x : represents an annealing temperature ($^{\circ}\text{C}$), and y : represents an annealing time (seconds)}.

21. (Amended) A production method of a plastic optical fiber, comprising the step of annealing a plastic optical fiber obtained by heat-drawing an undrawn fiber obtained by melt spinning, at a circumferential velocity ratio between (circumferential velocity of a rear roller / circumferential velocity of a front roller) between the front and rear rollers of 0.5 to 1.2 under heat conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$, wherein { T_{gc} : represents a glass transition temperature of a core, x : represents an annealing temperature ($^{\circ}\text{C}$), and y : represents an annealing time (seconds)}, while a tension of 0.35×10^6 to 1.5×10^6 Pa is applied to the fiber.

(12)特許協力条約に基づいて公開された国際出願

(19) 世界知的所有権機関
国際事務局



(43) 国際公開日
2001 年 3 月 22 日 (22.03.2001)

PCT

(10) 国際公開番号
WO 01/20376 A1

(51) 国際特許分類: G02B 6/00

(21) 国際出願番号: PCT/JP00/06093

(22) 国際出願日: 2000 年 9 月 7 日 (07.09.2000)

(25) 国際出願の言語: 日本語

(26) 国際公開の言語: 日本語

(30) 優先権データ:
特願平11/255802 1999 年 9 月 9 日 (09.09.1999) JP
特願2000/58812 2000 年 3 月 3 日 (03.03.2000) JP
特願2000/68866 2000 年 3 月 13 日 (13.03.2000) JP

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(81) 指定国 (国内): AU, CA, JP, KR, US.

(84) 指定国 (広域): ヨーロッパ特許 (AT, BE, CH, CY, DE,
DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

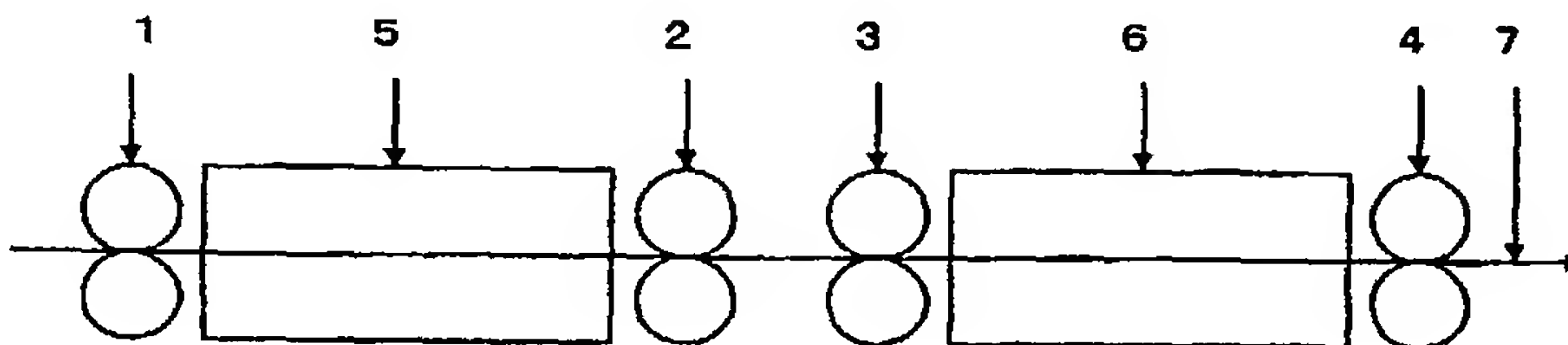
添付公開書類:

— 国際調査報告書

2文字コード及び他の略語については、定期発行される
各PCTガゼットの巻頭に掲載されている「コードと略語
のガイダンスノート」を参照。

(54) Title: PLASTIC OPTICAL FIBER, OPTICAL FIBER CABLE AND PLUG-ATTACHED OPTICAL FIBER CABLE AND
PRODUCTION METHODS THEREFOR

(54) 発明の名称: プラスチック光ファイバ、光ファイバケーブル及びプラグ付き光ファイバケーブル並びにこれら
の製造方法



(57) Abstract: A production method for plastic optical fibers, characterized by comprising the steps of heating/stretching non-stretched plastic optical fibers obtained by melt spinning, and then heat-treating the stretched fibers at a peripheral velocity ratio between front and rear rollers of at least 0.5 and up to 1.2 and under heating conditions satisfying the relations, $4 \leq y \leq -1.5x + 330$, $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$, [T_{gc} : glass transition temperature of core material, x : heat treating temperature ($^{\circ}\text{C}$), y : heat treating time (sec)], whereby plastic optical fibers small in heat shrinkage and excellent in heat resistance are provided.

[続葉有]

WO 01/20376 A1

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DESCRIPTION

Plastic Optical Fiber, Optical Fiber Cable, Plugged Optical Fiber Cable, and Production Methods thereof

5

Technical Field

The present invention relates to a plastic optical fiber, an optical fiber cable and a plugged optical fiber cable which are excellent in heat resistance, and production methods thereof.

10

Background Art

Heretofore, as an optical fiber, an inorganic glass optical fiber capable of excellent optical transmission over a wide wavelength range has been known and practically used mainly in a trunk line system. However, the inorganic glass optical fiber is expensive, has poor workability, and is not so resistant to bending stress. Therefore, a plastic optical fiber which is less expensive and in which making diameter large, the work of end faces and handling are easy has been developed and put to practical use in some fields of lighting, sensors, and wiring for communication between OA or FA equipment.

Generally, a plastic optical fiber (hereinafter referred to as "POF") is a fiber comprising a core-sheath structure in which as a core, a polymer having a large refractive index and excellent light transmittance such as polymethyl methacrylate, polycarbonate, polystyrene or

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amorphous polyolefin and a transparent polymer having a smaller refractive index than that of the core polymer as a sheath are used.

As a industrial production process of such a POF, in general, a core polymer and a sheath polymer are arranged concentrically by use of a multi-component fiber spinning nozzle and melt-spun into a fiber, and the fiber is then drawn under heating for improving mechanical strength.

Of cores to be used in the POF, polymethyl methacrylate is used as a core of a high-performance POF on an industrial scale since it is excellent in transparency, mechanical strength and weather resistance.

However, since the glass transition temperature (hereinafter referred to as "Tg") of polymethyl methacrylate is as high as 100 to 115°C, its application is limited in view of heat resistance.

For this reason, Japanese Patent Application Laid-Open No. 18608-1983, for example, proposes that a protective layer is further provided around a sheath layer to form a structure comprising three or more layers so as to improve heat resistance.

Further, Japanese Patent Application Laid-Open No. 11128-1993 discloses a technique which improves uniformity in the diameter of a POF by suppressing fluctuations in the diameter of the POF when it is subjected to heat drawing or an annealing after the heat drawing.

Further, Japanese Patent Application Laid-Open No.

16905-1992 discloses a method of improving a transmission loss by heating a POF having a polycarbonate as a core at 60 to 100°C for a long time.

However, the method disclosed in Japanese Patent Application Laid-Open No. 16905-1992 cannot improve the heat resistance of a POF since the annealing temperature is lower than the Tg of the core by 50°C or more and the annealing time is short. Further, the invention disclosed in Japanese Patent Application Laid-Open No. 18608-1983 has the problem that even if the heat resistance of a material used in the protective layer is improved, a core itself is thermally shrunk when the temperature used gets close to the Tg of the core. Further, Japanese Patent Application Laid-Open No. 11128-1993 is about the internal structure of a heating furnace used for the annealing, and since an appropriate annealing time and tension when a POF is heated at a predetermined annealing temperature are not set, the effect of reducing the thermal shrinkage of a POF is not satisfactory.

In addition, to improve the properties such as heat resistance of a POF, Japanese Patent Application Laid-Open Nos. 131206-1987, 303304-1988, 68503-1990, 201270-1994, 299912-1987 and the like disclose a method in which a POF is subjected to a non-contact annealing in line after the drawing step to maintain orientation of polymer chains in the POF axial direction which has been provided in the drawing step as much as possible so as to suppress the

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glass transition temperature of a core) - 35]°C.

Further, the present invention relates to a plastic optical fiber cable obtained by forming a coating layer around the plastic optical fiber of the present invention.

5 Further, the present invention relates to a plugged plastic optical fiber cable obtained by attaching a plug on the tip of the plastic optical fiber cable of the present invention.

10 Further, the present invention relates to a method for producing a plastic optical fiber which comprises the steps of heat drawing an undrawn plastic optical fiber obtained by melt spinning and subjecting the drawn fiber to an annealing at a circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear
15 roller / circumferential velocity of a front roller) of 0.5 to 1.2 under heating conditions which satisfy $4 \leq y \leq 1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$ [T_{gc} : a glass transition temperature of a core, x : an annealing temperature (°C), and y : an annealing time (seconds)].

20 Further, the present invention relates to a method for producing a plastic optical fiber which comprises the step of conducting the annealing twice or more under the above heating conditions in the above production method of the present invention.

25 Further, the present invention relates to a method for producing a plastic optical fiber which comprises the step of heat treating a plastic optical fiber obtained by

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melt spinning at a temperature from (a glass transition temperature of a core - 5)°C to (a glass transition temperature of the core + 80)°C while a tension of 0.35×10^6 to 1.5×10^6 Pa is applied to the plastic optical fiber.

5 Further, the present invention relates to a method
for producing a plastic optical fiber cable which comprises
the steps of obtaining a plastic optical fiber by the above
method of the present invention and forming a coating layer
around the obtained optical fiber.

10 Furthermore, the present invention relates to a
method for producing a plugged plastic optical fiber cable
which comprises the steps of obtaining a plastic optical
fiber by the above method of the present invention and
attaching a plug on the tip of the obtained optical fiber
15 cable.

According to the present invention, a plastic optical fiber, an optical fiber cable and a plugged optical fiber cable which have a small shrinkage ratio and excellent heat resistance can be provided.

20

Brief Description of the Drawings

Fig. 1 is a diagram for illustrating a method of determining a shrinkage stress occurring temperature of a plastic optical fiber and a graph indicating changes in stress against temperature and obtained by thermomechanical analysis.

Fig. 2 is a diagram showing an example of a DSC

curve in the vicinity of the Tg of a core.

Fig. 3 is a schematic block diagram showing a production device 1 used in the present invention.

Fig. 4 is a schematic block diagram showing a
5 repeated bending tester.

Fig. 5 is a schematic block diagram showing a production device 2 used in the present invention.

Fig. 6 is a schematic block diagram showing a production device 3 used in the present invention.

10 Fig. 7 is a schematic block diagram showing a production device 4 used in the present invention.

Fig. 8 is a schematic block diagram showing a perforated plate in a production device used in the present invention.

15 Fig. 9 is a schematic block diagram showing a production device used in the present invention which has a perforated plate disposed therein.

Best Mode for Carrying Out the Invention

20 Preferred embodiments of the present invention will be described hereinafter. A glass transition temperature of a core constituting a POF will be indicated as "Tgc" as appropriate.

In the present invention, a POF having excellent
25 heat resistance can be obtained by setting the shrinkage stress occurring temperature of the POF to be (Tgc - 35)°C or higher (first invention).

Further, in the present invention, the heat resistance of the POF of the first invention can be further improved by, in particular, using a homopolymer of methyl methacrylate as the core of the POF and setting the absolute
5 value of the birefringence of the core at 2.0×10^{-4} or smaller.

Further, in the present invention, the heat resistance of the POF of the first invention can be further improved and a decrease in the mechanical strength of the
10 POF can be reduced by using a homopolymer of methyl methacrylate as the core of the POF, setting the shrinkage stress occurring temperature obtained by thermomechanical analysis of the POF to be (the glass transition temperature of the core - 20) °C or higher and setting the absolute value
15 of the birefringence of the core to be 1.5×10^{-4} or larger.

Further, in the present invention, a POF having excellent heat resistance can be obtained because an undrawn POF obtained by melt spinning is heat-drawn and then subjected to an annealing at a circumferential velocity
20 ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of 0.5 to 1.2 under heating conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$ [T_{gc}: a glass transition temperature of a core, x: an
25 annealing temperature (°C), and y: an annealing time (seconds)] (second invention).

Further, in the present invention, in the production

method of a POF of the second invention, a POF having better heat resistance and mechanical strength can be obtained by using a homopolymer of methyl methacrylate as the core, carrying out the above heat drawing such that the absolute
5 value of the birefringence of the core would become 3×10^{-4} or larger and carrying out the above annealing at a circumferential velocity ratio between the front and rear rollers (circumferential velocity of the rear roller / circumferential velocity of the front roller) of 1 or less
10 under conditions which satisfy $x \leq (T_{gc} + 20)^{\circ}\text{C}$ [T_{gc} : the glass transition temperature of the core, x : an annealing temperature ($^{\circ}\text{C}$)].

Further, in the present invention, a POF having further improved heat resistance can be obtained by carrying
15 out the above annealing twice or more under the above heating conditions (third invention).

Further, in the present invention, a POF having improved heat resistance can be obtained by heat treating a POF obtained by melt spinning at temperatures from ($T_{gc} -$
20 $5)^{\circ}\text{C}$ to $(T_{gc} + 80)^{\circ}\text{C}$, preferably after the POF is heat-drawn, while applying a tension of 0.35×10^6 Pa to 1.5×10^6 Pa to the POF (fourth invention).

As the core of the POF of the present invention, a transparent amorphous polymer is suitable. Particularly, a
25 homopolymer of methyl methacrylate or a copolymer comprising a methyl methacrylate unit and another monomer unit (hereinafter referred to as "MMA polymer" as required) is

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preferably used. As other materials usable as the core of the POF, a copolymer comprising a unit of monomer such as a methacrylic acid ester as exemplified by cyclohexyl methacrylate, t-butyl methacrylate, isobornyl methacrylate, 5 adamantyl methacrylate, benzyl methacrylate, phenyl methacrylate or naphthyl methacrylate and a unit of monomer copolymerizable with these monomers, a polycarbonate, a polystyrene, a styrene-methacrylate copolymer, or deuterides of these polymers which are obtained by substituting all or 10 some of hydrogen atoms of the above polymers with deuterium atoms can be used. As a matter of course, other transparent polymers and transparent blends can also be used.

An MMA polymer, particularly a homopolymer of methyl methacrylate, has a wider temperature range in which it can 15 remain in a rubber state than other transparent amorphous materials, particularly a polycarbonate. Since it never happens that the MMA polymer becomes stiff and can hardly be drawn at temperatures lower than a certain temperature or that it becomes suddenly too stretchable at temperatures 20 higher than a certain temperature, the MMA polymer can be drawn or annealed in good condition. Further, since its orientation is not loosened as easily as that of a polycarbonate in particular, its tension is not lowered by heat easily. Therefore, even when the annealing is carried 25 out with low tension, the annealing can be carried out stably and non-uniformity in the diameter of a fiber is not worsened easily. Further, since the orientation is not

loosened easily, it is not necessary to adjust an annealing temperature to an excessively low temperature so as not to loosen the orientation, so that the MMA polymer can be heat treated in a moderately viscoelastic state. As a result, a
5 desired annealing effect can be obtained to a sufficient degree without degrading other properties of a POF such as non-uniformity in the diameter of the fiber. Particularly, when the annealing is carried out with low tension as in the fourth invention, a POF using an MMA polymer as a core is
10 suitable.

As a copolymer comprising a methyl methacrylate unit and another monomer unit, a copolymer comprising at least 70% by weight of methyl methacrylate unit and at most 30% by weight of the other monomer unit based on 100% by weight of
15 all monomer units is preferred. Illustrative examples of monomers copolymerizable with methyl methacrylate include methacrylic acid esters such as cyclohexyl methacrylate, isobornyl methacrylate, benzyl methacrylate, phenyl methacrylate and 2,2,2-trifluoroethyl methacrylate, acrylic
20 esters such as methyl acrylate and ethyl acrylate, and maleimide compounds intended for improving heat resistance such as N-cyclohexylmaleimide and N-isopropylmaleimide.

A method for producing the core is not particularly limited, and a known polymerization method is used. However,
25 to prevent foreign substrates from mixing into the core, a continuous bulk polymerization method or a continuous solution polymerization method is preferably used.

Illustrative examples of materials suitably used in the sheath of the POF of the present invention from the viewpoint of transmission characteristics include a homopolymer of a fluorine-based methacrylate, a copolymer comprising a fluorine-based methacrylate unit and a methacrylic ester monomer unit, a copolymer containing a vinylidene fluoride unit as a main component such as a vinylidene fluoride-tetrafluoroethylene copolymer, an α -fluoromethacrylate, and mixtures thereof.

As the structure of the POF of the present invention, a known structure can be used. Illustrative examples of a POF having such a known structure include a POF having a two-layer structure comprising a core and a sheath, a graded index-type POF whose core has refractive index distribution, a multi-core POF having a sea-island structure in which a plurality of island components each comprising a core and a sheath are disposed in a sea component, a multi-core POF having a structure in which a plurality of cores are collected in a sheath, and a multilayer POF whose core or sheath has a multilayer structure and whose refractive index gradually changes from the center toward the periphery.

A protective layer having such properties as solvent resistance and heat resistance may be formed on the peripheries of these POFs. As a material (protective material) used in the protective layer, a material having excellent mechanical strength is preferably used, and a vinylidene fluoride-tetrafluoroethylene copolymer is

particularly preferably used. The vinylidene fluoride-
tetrafluoroethylene copolymer has high adhesion to a polymer
used as a sheath and comprising a fluorine-based
methacrylate unit or a vinylidene fluoride unit or Nylon 12
5 which is suitably used in a coating layer in such an
application that requires heat resistance in particular.
Therefore, together with the characteristic of the POF of
the present invention that it has small shrinkage in a high-
temperature environment, a POF cable obtained by forming a
10 protective layer comprising a vinylidene fluoride-
tetrafluoroethylene copolymer around the POF of the present
invention having a core-sheath structure in which the sheath
comprises a polymer comprising a fluorine-based methacrylate
unit or a vinylidene fluoride unit and by forming a coating
15 layer comprising Nylon 12 on the protective layer can
significantly reduce the pistoning phenomenon in a high-
temperature environment of the POF cable.

A POF melt-spun by use of a material as described
above is preferably heat-drawn for the purpose of improving
20 its mechanical strength. As a drawing device, one having a
heating furnace disposed between a front roller and a rear
roller can be used, for example. Although an appropriate
heating temperature (drawing temperature) at the time of
drawing is set according to the physical properties of a
25 core, the temperature is preferably $(T_{gc} + 5)^{\circ}\text{C}$ to $(T_{gc} + 65)^{\circ}\text{C}$, more preferably $(T_{gc} + 10)^{\circ}\text{C}$ to $(T_{gc} + 60)^{\circ}\text{C}$. When
the drawing temperature is out of the above temperature

range, that is, lower than $(T_{gc} + 5)^{\circ}\text{C}$, the POF may become difficult to stretch. On the other hand, when the drawing temperature is higher than $(T_{gc} + 65)^{\circ}\text{C}$, sufficient mechanical strength may not be imparted to the POF by drawing. When the core is a PMMA, the drawing temperature is preferably 115°C or higher, more preferably 120°C or higher, much more preferably 125°C or higher, also is preferably 185°C or lower, more preferably 180°C or lower, much more preferably 175°C or lower.

The drawing ratio in the heat drawing is preferably 1.1 to 3.5 times (the circumferential velocity ratio between the front and rear rollers (circumferential velocity of the rear roller / circumferential velocity of the front roller) is 1.1 to 3.5), more preferably 1.5 to 3.3 times, much more preferably 1.5 to 3.0 times. When the drawing ratio is out of the above range, that is, smaller than 1.1 times, sufficient mechanical strength may not be imparted to the POF by drawing. On the other hand, when the drawing ratio is larger than 3.5 times, it may become difficult to carry out uniform drawing.

Thus, in the production of the POF, drawing is generally carried out for improving the mechanical strength of the POF. However, while the molecules of the POF are oriented by drawing the POF, stress (inner strain) different from orientation remains and is fixed in the POF. Therefore, as the temperature of the POF is increased to a temperature close to the T_{gc} of the POF, the fixed residual stress

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(inner strain) is released, thereby causing the POF to shrink significantly.

The degree of such stress (inner strain) remaining in a POF can be known by means of thermomechanical analysis. That is, when a POF is subjected to thermomechanical analysis as the temperature of the POF is increased at a fixed speed, fixed residual stress is released at a given temperature, thereby causing shrinkage stress. A POF having less residual stress has a shrinkage stress occurring temperature shifted to a higher temperature side. Thus, a POF having a high shrinkage stress occurring temperature is a POF having a small thermal shrinkage ratio and excellent heat resistance.

In the present invention, a POF is heat-treated under given conditions to remove residual stress from the POF, thereby reducing the thermal shrinkage of the POF and improving the heat resistance of the POF.

The POF of the present invention has a shrinkage stress occurring temperature obtained by thermomechanical analysis (TMA) of not lower than $(T_{gc} - 35)^{\circ}\text{C}$ (first invention). Such a POF has a low thermal shrinkage ratio and exhibits excellent heat resistance accordingly. The higher the shrinkage stress occurring temperature the better it is. However, it is generally lower than or equal to the T_{gc} . When a POF is applied to such an application as interior wiring of an automobile, it is required to be heat resistant at least at 90°C . A POF which has excellent heat

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resistance, that is, exhibits a thermal shrinkage ratio of not higher than 2% in a heat resistance test conducted at 90°C for 65 hours can be obtained by setting the shrinkage stress occurring temperature of the POF to be not lower than
5 (T_{gc} - 35)°C as in the present invention.

The shrinkage stress occurring temperature can be determined from the shrinkage stress curve shown in Fig. 1 as described later. Further, since the result of the thermomechanical analysis is apt to slightly change
10 according to measurement conditions, the thermomechanical analysis is carried out at a temperature rising rate of 5°C/min under a constant load of 2.2×10^5 Pa in the present invention.

A thermal shrinkage ratio which is an indicator of
15 the heat resistance of the POF of the present invention is a thermal shrinkage ratio in the longitudinal direction of the POF. A POF having a smaller thermal shrinkage ratio has better heat resistance. The measurement of the thermal shrinkage ratio is carried out in the following manner. A
20 POF is marked at an interval (L_0) of 50 cm in advance, and the POF is hung in a hot air dryer set at 90°C without contacting walls, shelves and the like in the hot air dryer. After 65 hours, the POF was taken out of the dryer and left standing to cool to room temperature (20°C). Then, an
25 interval (L_1) between the marks is measured, and a thermal shrinkage ratio is calculated from the L_0 and L_1 by use of the following equation.

$$\text{Thermal shrinkage Ratio (\%)} = [(L_0 - L_1)/L_0] \times 100$$

Further, in the present invention, a POF having a reduced thermal shrinkage ratio and exhibiting excellent heat resistance accordingly can be obtained by using a homopolymer of methyl methacrylate as a core of the POF and setting the birefringence absolute value of the core to be not larger than 2.0×10^{-4} .

As described above, heat drawing is carried out for imparting mechanical strength to a POF. An example of an indicator for molecular orientation of a core which is caused by stretch of a POF is birefringence of the core. The value of the birefringence may be positive or negative depending on a material used as a core. The larger the absolute value of the birefringence, the higher the degree of molecular orientation and the mechanical strength of a POF. However, as the absolute value of the birefringence becomes larger, residual stress (inner strain) fixed in a POF which degrades the heat resistance of the POF also increases. In the present invention, the birefringence of a core of a POF may be adjusted so as to relax the residual inner strain in the POF and improve the heat resistance of the POF. In the case of a POF having a core comprising a homopolymer of methyl methacrylate, when the absolute value of birefringence becomes 2.0×10^{-4} or smaller, its thermal shrinkage ratio becomes small and heat resistance improves. Therefore, when prime importance is placed on the heat resistance of the POF of the present invention which has a

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core comprising a homopolymer of methyl methacrylate, the birefringence absolute value of the core is preferably not larger than 2.0×10^{-4} , more preferably 0.5×10^{-4} to 2.0×10^{-4} . When the birefringence absolute value of the core
5 becomes smaller than 0.5×10^{-4} , its mechanical strength may be degraded.

A POF which has a core comprising a homopolymer of methyl methacrylate and having a birefringence absolute value of not larger than 2.0×10^{-4} , though depending on the
10 physical properties of the used homopolymer of methyl methacrylate, can be obtained by subjecting the POF to the annealing to be described later. The birefringence is measured in the manner to be described later.

As described above, the mechanical strength of a POF
15 can be improved by drawing the POF to impart molecular orientation so as to increase the absolute value of the birefringence of a core. However, at the same time, the degree of its thermal shrinkage also becomes greater. In the present invention, the birefringence of a core and the
20 thermal shrinkage stress occurring temperature of a POF can be set to be within predetermined ranges so that thermal shrinkage and a decrease in mechanical strength can be reduced. For example, in the case of a POF having a core comprising a homopolymer of methyl methacrylate, the POF
25 preferably has a birefringence absolute value of not lower than 1.5×10^{-4} and a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than (Tgc

- 20)°C since sufficient mechanical strength and anti thermal shrinkability can be imparted to the POF. More preferably, the absolute value of the birefringence is not lower than 2.3×10^{-4} and the shrinkage stress occurring temperature is not lower than (Tgc - 15)°C. When the absolute value of the birefringence is too high, it is difficult to have a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than (Tgc - 20)°C. Therefore, the absolute value of the birefringence is preferably not higher than 5×10^{-4} . Such a POF can exhibit a thermal shrinkage ratio of not higher than 0.5% in a heat resistance test conducted at 90°C for 65 hours, and the number of repeated bending counted for a POF cable which is obtained by forming a coating layer composed of a polyethylene around the POF and has an outside diameter (thickness of the coating layer: 0.6 mm) of 2.2 mm can be at least 10,000 times. Further, the number of repeated bending counted for a POF cable which is obtained by forming a coating layer composed of Nylon 12 around the POF and has an outside diameter (thickness of the coating layer: 0.6 mm) of 2.2 mm can be at least 20,000 times. The coating layer composed of Nylon 12 can be coated twice or more as required. The number of repeated bending is counted by a method to be described later. A POF with a larger number of repeated bending has better mechanical strength.

In the production method (second invention) of a POF of the present invention, a drawn POF is heat-treated at a

circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of 0.5 to 1.2 under heating conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$. Thereby, internal stress (inner strain) fixed and remaining in the POF is partially relaxed, and a POF having a smaller thermal shrinkage ratio and better heat resistance than a POF not subjected to such an annealing can be obtained. By the production method of the present invention, a POF having a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than $(T_{gc} - 35)^{\circ}\text{C}$ can be obtained, and a POF which exhibits a thermal shrinkage ratio of not higher than 2% in a heat resistance test conducted at 90°C for 65 hours. Further, when a homopolymer of methyl methacrylate is used as a core, a POF which has a core having a birefringence absolute value of not higher than 2.0×10^{-4} and has excellent heat resistance can be obtained. Further, when a homopolymer of methyl methacrylate is used as a core, a POF which has a core having a birefringence absolute value of not lower than 1.5×10^{-4} and has a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than $(T_{gc} - 20)^{\circ}\text{C}$, that is, a POF having excellent heat resistance and mechanical strength can be obtained. In this case, the absolute value of the birefringence of the core is preferably not lower than 2.3×10^{-4} , and the shrinkage

stress occurring temperature obtained by thermomechanical analysis is preferably not lower than $(T_{gc} - 15)^{\circ}\text{C}$.

When the circumferential velocity ratio (circumferential velocity of the rear roller/circumferential velocity of the front roller) is smaller than 1, the obtained POF is shrunk. In view of the possibility that too large shrinkage may cause a decrease in molecular orientation imparted by drawing and in turn a degradation in the mechanical strength of the POF, the possibility that productivity may be decreased since it takes long time to have large shrinkage, and the possibility that the mechanical strength of the POF may be further degraded since the POF is heated at high temperatures not lower than $(T_{gc} - 5)^{\circ}\text{C}$ during the long time period, a circumferential velocity ratio of not smaller than 0.5 is used. On the other hand, when the circumferential velocity ratio exceeds 1.2, an effect of improving heat resistance according to the present invention is not exhibited to a sufficient degree.

Further, in the present invention, the annealing is carried out under heating conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$. When an annealing temperature x is out of the above temperature range, an effect of improving heat resistance by the annealing becomes less sufficient as the annealing temperature becomes lower than $(T_{gc} - 5)^{\circ}\text{C}$, while the annealing temperature is larger than $(T_{gc} + 110)^{\circ}\text{C}$, mechanical strength imparted by drawing may be degraded.

The annealing temperature x is preferably $(T_{gc} + 90)^{\circ}\text{C}$ or lower, more preferably $(T_{gc} + 75)$ or lower. Also, the annealing temperature x is preferably $T_{gc}^{\circ}\text{C}$ or higher, more preferably $(T_{gc} + 15)^{\circ}\text{C}$ or higher.

5 When a core is polymethylmethacrylate, the annealing temperature x is preferably 110°C or higher, more preferably 115°C or higher. Also, the annealing temperature x is preferably 200°C or lower, more preferably 190°C or lower. Meanwhile, when the annealing time y is less than 4
10 seconds, an effect of improving heat resistance by the annealing becomes insufficient, while when the annealing time y is more than $(-1.5x + 330)$ seconds, mechanical strength imparted by drawing is degraded. In the present invention, the annealing time is calculated from the
15 following equation:

$$\text{The annealing time (min)} = 2s / (v_1 + v_2)$$

In the above equation, s indicates a furnace length (m) of a heating furnace, v_1 a circumferential velocity (m/min) of a front roller, and v_2 a circumferential velocity (m/min) of a
20 rear roller.

As a heating furnace used in conducting the annealing, a non-contact heating furnace is preferably used for protecting a POF from being damaged. A heating furnace using hot air as a heating medium or a moist heating furnace
25 using pressurized steam as a heating medium can be used.

Further, in the production method (second invention) of the present invention, a homopolymer of methyl

methacrylate is preferably used as a core, a POF is preferably heat-drawn such that the absolute value of the birefringence of the core would be not smaller than 3×10^{-4} , and the subsequent annealing is preferably carried out at a

5 circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of not larger than 1 and an annealing temperature of not higher than $(T_{gc} + 20)^{\circ}\text{C}$. The heat drawing is preferably carried out such

10 that the absolute value of the birefringence of the core would be not larger than 6×10^{-4} in view of a load to be imposed on the subsequent annealing. When the core of the heat-drawn POF has a birefringence absolute value of not smaller than 3×10^{-4} , molecular orientation caused by heat

15 drawing can be imparted to a sufficient degree. When the circumferential velocity ratio between the front and rear rollers at the time of the annealing conducted after the heat drawing is not larger than 1, a shrinkage stress occurring temperature can be increased and thermal shrinkage

20 can be reduced. When the annealing temperature is set to be relatively low, i.e., not higher than $(T_{gc} + 20)^{\circ}\text{C}$, a decrease in molecular orientation caused by the annealing can be minimized. That is, by carrying out heat drawing and the annealing under such conditions, sufficient mechanical

25 strength and anti thermal shrinkability can be imparted to a POF, whereby a POF which has a shrinkage stress occurring temperature obtained by thermomechanical analysis of not

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lower than $(T_{gc} - 20)^{\circ}\text{C}$ and has a core having a birefringence absolute value of not lower than 1.5×10^{-4} can be obtained. Further, by producing the POF under the above conditions, the thermal shrinkage ratio of the POF can be 0.5% or smaller, the number of repeated bending counted when a coating layer composed of a polyethylene is formed around the POF can be at least 10,000 times, and the number of repeated bending counted when a coating layer composed of Nylon 12 is formed around the POF can be at least 20,000 times as described above. A plurality of coating layers can be coated as required.

In the present invention, a POF is preferably heat-treated while a tension of 0.35×10^6 to 1.5×10^6 Pa, preferably 0.35×10^6 to 1.35×10^6 Pa is applied to the POF. When the tension is smaller than 0.35×10^6 Pa, the POF makes contact with an annealing device at the time of the annealing, so that the annealing may not be able to be carried out stably. On the other hand, when it is larger than 1.5×10^6 Pa, an effect of improving heat resistance by the annealing may be insufficient. The tension at the time of the annealing can be adjusted by setting an annealing temperature, a flow rate of a heating medium used in the annealing and a circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of a heating furnace at the time of the annealing to be proper values.

Further, in the production method (second invention) of the present invention, when the annealing is carried out while tension is applied to a POF as described above, the tension is preferably not larger than 1.35×10^6 Pa, an
 5 annealing temperature is preferably $(T_{gc} - 5)^\circ\text{C}$ to $(T_{gc} + 15)^\circ\text{C}$, and the annealing time preferably satisfies $10 \leq y \leq -1.5x + 330$ [x: an annealing temperature ($^\circ\text{C}$), and y: an annealing time (seconds)]. By carrying out the annealing under such conditions, a POF having a birefringence absolute
 10 value of not lower than 2.3×10^{-4} and a shrinkage stress occurring temperature of not lower than $(T_{gc} - 15)^\circ\text{C}$ can be obtained.

In the above production method, a drawing step and an annealing step may be carried out in a continuous process.
 15 Alternatively, a drawn POF may be wound around a bobbin, and then the POF may be heat-treated.

Further, in the production method of a POF according to the present invention, heat resistance can be improved by carrying out the annealing twice or more under the above
 20 heating conditions of the above production method (second invention) (third invention). Thereby, inner strain (internal stress) fixed and remaining in a POF is partially relaxed, and a POF having a smaller thermal shrinkage ratio and better heat resistance than a POF not subjected to such
 25 an annealing or a POF subjected to the annealing only once can be obtained. In this case, an annealing temperature x is preferably not lower than T_{gc} $^\circ\text{C}$. When a POF having a

shrinkage stress occurring temperature of not lower than
(T_{gc} - 35)°C is produced by the method (third invention) of
the present invention, a thermal shrinkage ratio of not
higher than 2%, or even not higher than 1.5%, can be
5 achieved in a heat resistance test conducted at 90°C for 65
hours. Further, when a homopolymer of methyl methacrylate
is used as a core, a POF with a core having a birefringence
absolute value of not larger than 2.0×10^{-4} can be obtained.

The annealing which satisfies the above heating
10 conditions is preferably carried out twice to six times.
When the annealing is carried out at least twice, heating
can be done to a sufficient degree without increasing a
heating furnace length. Further, when the annealing is
carried out six times at the maximum, the constitution of
15 the device becomes relatively simple. This annealing may be
repeated under the same conditions or different conditions.
A heating furnace used in the annealing and heating
conditions at the time of the annealing are the same as
those of the above production method (second invention) and
20 are set as appropriate according to the number of times the
annealing is carried out.

In the production method of the present invention, a
drawing step and the annealing may be carried out in a
continuous process. Alternatively, after the drawing step
25 and a first annealing are carried out in a continuous
process, the subsequent annealing may be carried out after a
drawn POF may be wound around a bobbin. Alternatively, a

drawn POF may be wound around a bobbin, and then the POF may be subjected to the annealing. Alternatively, a method in which a drawn POF is caused to move back and force in an annealing device can also be used.

5 In the present invention (fourth invention), a POF obtained by melt spinning is heat-treated at temperatures ranging from $(T_{gc} - 5)^{\circ}\text{C}$ to $(T_{gc} + 80)^{\circ}\text{C}$ while a tension of 0.35×10^6 to 1.5×10^6 Pa, preferably 0.35×10^6 to 1.35×10^6 Pa, is applied to the POF, thereby removing inner strain
10 fixed in the POF and obtaining a POF having excellent heat resistance. According to this method, the POF of the first invention, that is, a POF having a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than $(T_{gc} - 35)^{\circ}\text{C}$ can be obtained. Further, a
15 POF which exhibits a thermal shrinkage ratio of not higher than 2% in a heat resistance test conducted at 90°C for 65 hours can be obtained. Further, when a homopolymer of methyl methacrylate is used as a core, a POF with a core having a birefringence absolute value of not larger than 2.0×10^{-4}
20 $\times 10^{-4}$ can be obtained. Further, when a homopolymer of methyl methacrylate is used as a core, a POF which has a core having a birefringence absolute value of not smaller than 1.5×10^{-4} and has a shrinkage stress occurring temperature obtained by thermomechanical analysis of not
25 lower than $(T_{gc} - 20)^{\circ}\text{C}$ can be obtained.

The above annealing is preferably carried out after an undrawn POF obtained by melt spinning is subjected to

heat drawing.

In the above annealing, when the tension is smaller than 0.35×10^6 Pa, the POF may make contact with an annealing device at the time of the annealing, so that the annealing may become unstable, while when it is larger than 1.5×10^6 Pa, an effect of improving heat resistance by the annealing is insufficient. The tension at the time of the annealing can be adjusted by setting an annealing temperature, a flow rate of a heating medium used in the annealing and a circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of a heating furnace at the time of the annealing to be proper values.

The annealing temperature is $(T_{gc} - 5)^\circ\text{C}$ to $(T_{gc} + 80)^\circ\text{C}$, preferably $(T_{gc} - 5)^\circ\text{C}$ to $(T_{gc} + 60)^\circ\text{C}$, more preferably $(T_{gc} - 5)^\circ\text{C}$ to $(T_{gc} + 30)^\circ\text{C}$, particularly preferably $T_{gc}^\circ\text{C}$ to $(T_{gc} + 15)^\circ\text{C}$. When the annealing temperature is out of the above range, that is, lower than $(T_{gc} - 5)^\circ\text{C}$, an improving effect caused by the annealing is insufficient. On the other hand, when the annealing temperature is higher than $(T_{gc} + 80)^\circ\text{C}$, mechanical properties may be degraded due to relax of orientation imparted by drawing.

To improve heat resistance significantly without degrading mechanical strength in the annealing, it is preferable to use a polymer containing a methyl methacrylate

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unit in an amount of at least 70% by weight as a core of a POF. Particularly, when a POF with a core comprising a homopolymer of methyl methacrylate is heat-treated at temperatures ranging from $(T_{gc} - 5)^{\circ}\text{C}$ to $(T_{gc} + 30)^{\circ}\text{C}$,
5 preferably temperatures not higher than $(T_{gc} + 15)^{\circ}\text{C}$ while a tension of 0.35×10^6 to 1.5×10^6 Pa, preferably a tension of not larger than 1.35×10^6 Pa is applied to the POF, a POF which has a core having a birefringence absolute value of not lower than 1.5×10^{-4} , preferably not lower than $2.3 \times$
10 10^{-4} and has a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than $(T_{gc} - 20)^{\circ}\text{C}$, preferably not lower than $(T_{gc} - 15)^{\circ}\text{C}$, that is, a POF having mechanical strength and heat resistance can be obtained. Further, by producing the POF under the above
15 conditions, the thermal shrinkage ratio of the POF can be 0.5% or smaller, the number of repeated bending counted when a coating layer composed of a polyethylene is formed around the POF can be at least 10,000 times, and the number of repeated bending counted when a coating layer composed of
20 Nylon 12 is formed around the POF can be at least 20,000 times as described above. A plurality of coating layers can be coated as required.

For the annealing of a POF, a known method such as a hot air method, a moist heating method or a hot water method
25 can be used. When hot air is used in the annealing, the higher the velocity of the hot air the more preferable it is, from the viewpoint of heating efficiency. However, the

velocity of the hot air is generally set to be 2 to 10 m/s. When the velocity of the hot air is lower than 2 m/s, heating efficiency becomes insufficient, whereby the heat resistance of the POF may not be able to be improved to a sufficient degree. On the other hand, when the velocity of the hot air is higher than 10 m/s, the POF sways in a heating furnace, whereby the quality of the POF may be degraded. In this case, the sway of the POF can be prevented effectively by coinciding the heading direction of the hot air with the heading direction of the POF.

Tension applied to a POF at the time of the annealing varies according to the temperature of the POF at the time of the annealing. The temperature of the POF is determined by an annealing temperature, a flow rate of a heating medium and the like. When the temperature of the POF at the time of the annealing is increased, tension tends to increase since the POF is shrunk. However, when the temperature is too high, orientation is further relaxed, thereby causing the tension to lower.

This annealing may be a fixed-length treatment (circumferential velocity ratio of rollers is about 1) or an alleviation treatment (circumferential velocity ratio of rollers is less than 1). However, to carry out the annealing under a tension of 0.35×10^6 to 1.5×10^6 Pa, the annealing is preferably the alleviation treatment. The alleviation treatment is preferably carried out at a circumferential velocity ratio between the front and rear

rollers (circumferential velocity of a rear roller /
circumferential velocity of a front roller) of 0.5 to 0.98,
more preferably 0.7 to 0.95, particularly preferably 0.8 to
0.95. When the circumferential velocity ratio is much

5 smaller than the above range, mechanical properties of a POF
may be degraded, while when the circumferential velocity
ratio is much larger than the above range, it becomes
difficult to have a tension applied to the POF of 0.35×10^6
to 1.5×10^6 Pa.

10 Further, in the present invention, the annealing can
be carried out by use of a heating furnace into which a POF
is introduced horizontally. However, when the annealing is
carried out under a tension of 0.35×10^6 to 1.5×10^6 Pa,
the POF may hang down in the furnace by its own weight and
15 make contact with the heating furnace in some cases. To
prevent this, a POF to be heat-treated is introduced into an
annealing zone substantially vertically to a horizontal
plane and heat-treated. To carry out the annealing in this
manner, an annealing device may be disposed perpendicularly
20 to the ground, for example.

Further, when a POF is heat-treated under a tension
of 0.35×10^6 to 1.5×10^6 Pa by use of a heating furnace
disposed substantially horizontally, the annealing can be
carried out with the POF to be heat-treated supported by a
25 heating medium which provides buoyancy to the POF to prevent
the POF from making contact with the heating furnace. For
example, a POF is heat-treated with the POF supported by a

heating medium such as hot air or pressurized steam blown out of pores of a porous plate such as a porous metal plate, porous heat-resistant plastic or porous sintered metal plate disposed in a heating furnace. In that case, to prevent the

5 POF to be heat-treated from swaying, a wedge-shaped or concave path for passing the POF may be formed on the porous plate so that the heating medium can also be blown out from the path. The shape of the pores of the porous plate may be circular or rectangular but is not limited to these. When

10 the pore is circular, its diameter is set as appropriate according to the annealing conditions and the size of a POF but is preferably 0.1 to 3 mm. When the diameters of the pores are too small, effects of the annealing and supporting a POF by a heating medium may be insufficient, while when

15 the diameters of the pores are too large, the flow rate of a heating medium may be insufficient, thereby making it difficult to support a POF.

A POF obtained by carrying out the annealing at temperatures ranging from $(T_{gc} - 5)^{\circ}\text{C}$ to $(T_{gc} + 80)^{\circ}\text{C}$ under

20 a tension of 0.35×10^6 to 1.5×10^6 Pa can achieve a thermal shrinkage ratio after heated at 90°C for 65 hours of not higher than 0.5%. It is desirable to set the above conditions as appropriate in order to obtain such a POF.

Further, in the present invention, measurement of

25 tension is carried out near an outlet of a heating furnace. For example, in the case of the production device shown in Fig. 5, the measurement is carried out between the roller 16

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and the heating furnace 18, that is, at the point
represented by reference numeral 20; in the case of the
production device shown in Fig. 6, the measurement is
carried out between the roller 22 and the heating furnace 23,
5 that is, at the point represented by reference numeral 25;
and in the case of the production device shown in Fig. 7,
the measurement is carried out between the guide 29 on the
side of outlet and the heating furnace 28, that is, at the
point represented by reference numeral 31. The
10 constitutions of the devices are not limited to these.

The heat resistance of a POF obtained by the above-
described production method (second, third or fourth
invention) of a POF can be further improved by subjecting
the POF to the annealing, preferably a batch-type fixed-
15 length annealing, at temperatures not higher than $(T_{gc} + 8)^{\circ}\text{C}$.

The annealing in this case can be carried out by a
known method such as a hot air method, a vacuum heating
method or a moist heating method can be used. An annealing
20 temperature is set as appropriate according to a material of
POF to be heat-treated and is preferably $(T_{gc} - 30)^{\circ}\text{C}$ or
higher, more preferably $(T_{gc} - 25)^{\circ}\text{C}$ or higher, much more
preferably $(T_{gc} - 15)^{\circ}\text{C}$ or higher, also is preferably $(T_{gc} + 8)^{\circ}\text{C}$ or lower,
more preferably $(T_{gc} + 5)^{\circ}\text{C}$ or lower, much
25 more preferably $(T_{gc} + 3)^{\circ}\text{C}$ or lower. Particularly, when a
homopolymer of methyl methacrylate is used as a core, the
annealing temperature is preferably 85°C or higher, more

preferably 90°C or higher, much more preferably 100°C or higher, also is preferably 123°C or lower, more preferably 120°C or lower, much more preferably 118°C or lower. When the annealing is carried out at an excessively high temperature, e.g., at a temperature higher than a T_g by 10°C or more, over several hours, mechanical strength imparted by drawing may be further degraded as the temperature and time of the annealing increase. On the other hand, when the annealing temperature is too low, an effect of improving heat resistance may become insufficient.

The annealing time is selected as appropriate. When an annealing temperature is low, it may take a very long time, e.g., two to three days, to obtain an effect of annealing. When the annealing temperature is close to a glass transition temperature, the effect is exhibited even after a half day.

The above-described POF (first invention) of the present invention and POFs produced by the above-described production methods (second, third and fourth inventions) of a POF of the present invention can be used as POF cables by forming a coating layer around these POFs. As a material constituting the coating layer, a nylon resin such as conventionally used Nylon 12, a polyvinyl chloride, a polychlorotrifluoroethylene copolymer, a polyethylene, a polyurethane, perprene or the like can be used.

In addition, the POF cable can be used as a plugged POF cable by attaching a plug on the tip of the POF cable.

A known plug can be used as the plug and attached by a known method.

Examples

The present invention will be described in more
5 detail with reference to examples hereinafter. Evaluation
methods and production devices used in the examples are as
follows. As for the horizontal and vertical axes shown in
Fig. 1, temperature and stress increase in the directions of
corresponding arrows.

10 <Thermomechanical analysis (TMA)>

TMA-SS100 manufactured by Seiko Instruments Inc. was
used as a measuring device. The temperature rising rate was
set at 5°C/min. And a Shrinkage stress under a static load
of 2.2×10^5 Pa was measured. A point of intersection of a
15 horizontal tangent to a point where stress starts to be on
the increase after the decrease and a tangent to a point
where the inclination of stress becomes maximum after it has
been on the increase was taken as shrinkage stress occurring
temperature as shown in Fig. 1.

20 <Measurement of Glass Transition Temperature>

DSC-220 manufactured by Seiko Instruments Inc. was
used. A sample was heated to 200°C at a temperature rising
rate of 10°C/min and kept at the temperature for 10 minutes
to be melted, and then quenched to 20°C and heated at a
25 temperature rising rate of 10°C/min again. From a DSC curve
indicating exothermic and endothermic behaviors at that time,
as shown in Fig. 2, a point of intersection of a straight

line obtained by extending a base line at lower temperature side than a stepwise transition portion where glass transition occurs to higher temperature side and a tangent to a point of the DSC curve where the inclination of the stepwise transition portion of the DSC curve becomes maximum was taken as the glass transition temperature (refer to page 54 of "NEW BASICS AND APPLICATIONS OF THERMAL ANALYSIS" (1989), edited by Japan Thermal Measurement Institute, published by REALIZE CO., LTD., for example).

10 <Measurement of Birefringence>

A POF was immersed in a solvent such as dimethyl sulfoxide to remove a sheath layer and a protective layer so as to expose a core. The birefringence of the core was measured at room temperature by use of a polarizing microscope (polarizing microscope OPTIPHOTI-POL of Nikon Corporation) and a Senarmont compensator. When a vinylidene fluoride-tetrafluoroethylene copolymer is used in a sheath layer or a protective layer, the sheath layer and the protective layer can be removed with ease by immersing a POF in dimethyl sulfoxide at room temperature (20°C) for about 10 seconds.

<Production Device 1>

An example of a production device used in the present invention is shown in Fig. 3. In Fig. 3, reference numerals 1, 2, 3 and 4 denote nip rollers which have the function of delivering or withdrawing a POF denoted by reference numeral 7 at a fixed speed. Reference numerals 5

and 6 denote a heating furnace in which a POF is heated by use of hot air. A melt-spun undrawn POF is drawn at a given circumferential velocity ratio set by adjusting the circumferential velocities of rollers 1 and 2 and then heat
5 treated between the rollers 3 and 4. Although this production device comprises a first drawing device and a second annealing device arranged in series, these devices may be arranged separately. Further, when the annealing is carried out twice or more, other annealing devices may be
10 disposed after the annealing device. Reference numeral 20 denotes a point where tension is measured.

<Count of Number of Repeated Bending>

The number of repeated bending was counted by means of a repeated bending tester shown in Fig. 4. A POF cable 8
15 having a diameter of 2.2 mm is hung between two rollers 9 disposed with a spacing of 2.3 mm therebetween and each having a radius of 15 mm. A weight 10 having a weight of 0.5 kg is attached to one end of the POF cable 8, and the other end is held by holding hardware 13. The holding
20 hardware 13 is attached to an arm which moves the holding hardware 13 along a virtual semicircle having the center at a point O shown in Fig. 4 and formed over the two rollers 9. The point O is a point located at a point of intersection of a straight line connecting the tops of the two rollers to
25 each other and the symmetry axis of the two rollers. To be more specific, the arm falls down to one of the rollers 9 from a vertical direction to a horizontal direction at the

center 0, returns to the vertical direction, falls down to the other roller 9, and returns to the vertical direction again. The arm repeated this reciprocating action. The reciprocating action is counted as one action. The POF cable is repeatedly bent 30 times per minute. A light source is disposed at one end of the POF cable 8, and a photodetector is disposed at the other end. An LED 11 having a wavelength of 660 nm is used as the light source, and an optical power meter 12 is used as the photodetector. The POF cable 8 is disposed such that the distance from the optical power meter 12 to the roller 9 would be 1.5 m and the distance from the roller 9 to the LED 11 would be 3.5 m. The number of repeated bending in this test is the number of bendings of the POF cable when a quantity of light detected by the optical power meter is lowered from an initial value by 1 dB. In each example, an average of the results of five tests is shown as the number of repeated bending.

<Production Device 2>

An example of a production device used in the present invention is shown in Fig. 5. In Fig. 5, reference numerals 14, 15 and 16 denote nip rollers which have the function of delivering or withdrawing a POF denoted by reference numeral 19 at a fixed speed. Reference numerals 17 and 18 denote a heating furnace in which a POF is heated by use of hot air. A melt-spun undrawn POF is drawn at a given circumferential velocity ratio set by adjusting the circumferential velocities of rollers 14 and 15 and then

heat treated between the rollers 15 and 16. Although this production device comprises a first drawing device and a second annealing device arranged in series, these devices may be arranged separately. Further, when the annealing is
5 carried out twice or more, other annealing devices may be disposed after the annealing device.

<Production Device 3>

An example of a production device used in the present invention is shown in Fig. 6. In Fig. 6, reference
10 numerals 21 and 22 denote nip rollers which have the function of delivering or withdrawing a POF denoted by reference numeral 24 at a fixed speed. Reference numeral 23 denotes a heating furnace in which a POF is heated by use of hot air. The present production device is constituted such
15 that hot air is blown into the heating furnace from its center and the hot air blown into the heating furnace returns to a hot air generator from both sides of the heating furnace. The POF is drawn or heat treated by adjusting the circumferential velocities of the rollers 21
20 and 22. Reference numeral 25 denotes a point where tension is measured.

<Production Device 4>

An example of a vertically disposed production device used in the present invention is shown in Fig. 7. In
25 Fig. 7, reference numerals 26 and 27 denote nip rollers which have the function of delivering or withdrawing a POF denoted by reference numeral 30 at a fixed speed. Reference

temperature of the obtained POF are shown in Table 1.

In Table 1, the symbol ○ is given to examples in which annealing conditions satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 5)^{\circ}\text{C}$ [T_{gc}: a glass transition temperature of a core, x: an annealing temperature (°C), and y: an annealing time (seconds)], and the symbol × is given to examples in which the annealing conditions do not satisfy these equations.

POFs obtained by the method (second invention) of the present invention, that is, POFs which satisfy the above annealing conditions, have a shrinkage stress occurring temperature of at least $(T_{gc} - 35)^{\circ}\text{C}$, that is, at least 77°C, and a thermal shrinkage ratio of not higher than 2% which is lower than those of the POFs of Comparative Examples. Therefore, they are excellent in heat resistance.

Table 1

	Annealing Conditions		Thermal Shrinkage Ratio (%)	Shrinkage Stress Occurring Temp. (°C)	Annealing Conditions
	Temp. (°C)	Time(sec)			
Comp.Ex.1	-	-	2.4	73	-
Comp.Ex.2	145	3	2.1	76	×
Example 1	145	6	2.0	79	○
Example 2	145	10	1.7	80	○
Example 3	145	15	1.2	84	○
Example 4	145	30	1.0	85	○
Comp.Ex.3	165	3	2.2	76	×
Example 5	165	6	1.9	77	○
Example 6	165	9	1.5	80	○
Comp.Ex.4	185	3	2.3	76	×
Example 7	185	5	1.5	78	○
Comp.Ex.5	190	3	2.2	74	×

(Comparative Example 6)

A POF having a fiber diameter of 1,000 μm and a core-sheath structure was produced in the same manner as in Comparative Example 1 except that the roller circumferential velocity ratio (circumferential velocity of the roller 2 / circumferential velocity of the roller 1) was set to be 3.0. The thermal shrinkage ratio of the obtained POF is shown in Table 2.

(Examples 8 to 13)

The POF obtained in Comparative Example 6 was heat treated at a temperature of the non-contact heating furnace 6 having a furnace length of 3 m of 165°C, a circumferential velocity ratio (circumferential velocity of the roller 4/circumferential velocity of the roller 3) of 1.0, and roller circumferential velocities which were adjusted such that an annealing time would be 10 seconds, and the POF was then wound around a bobbin (Example 8). Then, the POF obtained in Example 8 was heat treated under the same conditions as used in Example 8 (using only the second device shown in Fig. 3), and the resulting POF was wound around a bobbin (Example 9). Thus, annealing of the POF was repeated under the same conditions as used in Example 8 for the numbers of times shown in Table 2 to obtain POFs which undergone the annealing for a different number of times (Examples 10 to 13).

The thermal shrinkage ratios of the obtained POFs are shown in Table 2. As is obvious from Table 2, POFs

having smaller thermal shrinkage ratios and excellent heat resistance could be obtained by repeating the annealing twice or more.

5 Table 2

	Number of Repeated Annealing	Thermal Shrinkage Ratio (%)
Comp.Ex.6	-	2.1
Example 8	1	1.6
Example 9	2	1.3
Example 10	3	1.2
Example 11	4	1.0
Example 12	5	0.9
Example 13	6	0.8

(Examples 14, 15 and 16)

The POF obtained in Example 8 was subjected batch-
 10 type fixed-length annealing at 90°C for 20 hours by using a
 commercially available hot air dryer in a similar manner
 (Example 14). Similarly, the POFs obtained in Examples 10
 and 13 were subjected the batch-type fixed-length annealing
 (Examples 15 and 16). The results are shown in Table 3.
 15 POFs having further smaller thermal shrinkage ratios and
 excellent heat resistance could be obtained by the batch-
 type fixed-length annealing.

Table 3

	Thermal Shrinkage Ratio (%)	Remarks
Example 14	0.5	POF of Example 8 was subjected to the fixed-length annealing at 90°C for 20 hours.
Example 15	0.4	POF of Example 10 was subjected to the fixed-length annealing at 90°C for 20 hours.
Example 16	0.3	POF of Example 13 was subjected to the fixed-length annealing at 90°C for 20 hours.

As described above, POFs obtained by the method (second invention) of the present invention, that is, POFs which satisfy the above annealing conditions, have a shrinkage stress occurring temperature of at least (T_{gc} - 35)°C, that is, at least 77°C, and a thermal shrinkage ratio of not higher than 2% which is lower than those of the POFs of Comparative Examples. Therefore, POFs having excellent heat resistance could be obtained. Further, it is understood that POFs having smaller thermal shrinkage ratios and excellent heat resistance could be obtained by carrying out the fixed-length annealing.

(Examples 17 and 18)

Polymethyl methacrylate obtained by continuous bulk polymerization was used as a core. The T_g of the core was 112°C (DSC method, temperature rising rate: 10°C/min). A copolymer of 51 parts by weight of 2,2,2-trifluoromethyl methacrylate, 30 parts by weight of 1,1,2,2-

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tetrahydroperfluorodecyl methacrylate, 18 parts by weight of methyl methacrylate and 1 part by weight of methacrylic acid was used as a sheath. A copolymer of vinylidene fluoride/tetrafluoroethylene = 80/20 (mol%) was used as a
5 material for a protective layer.

An undrawn POF comprising a core, a sheath and a protective layer was prepared from these polymers by means of a melt spinning method. The obtained undrawn POF was drawn at a roller circumferential velocity ratio
10 (circumferential velocity of the roller 2 / circumferential velocity of the roller 1) of 2.7 by means of the drawing device (first device shown in Fig. 3) comprising the non-contact heating furnace 5 set at 160°C and having a furnace length of 2.5 m and the rollers 1 and 2 so as to obtain a
15 POF having a fiber diameter of 1,000 μm and a core-sheath-protective-layer structure.

After wound around a bobbin, the obtained POF was heat treated at annealing temperatures and roller circumferential velocity ratios (circumferential velocity of
20 the roller 4 / circumferential velocity of the roller 3) shown in Table 4 for annealing times shown in Table 4 by use of the second device shown in Fig. 3, i.e., the annealing device comprising the non-contact heating furnace 6 having a furnace length of 2.5 m and the rollers 3 and 4, to obtain
25 POFs having a fiber diameter of 1,000 μm and a core-sheath-protective-layer structure. The shrinkage stress occurring temperatures, birefringence absolute values and thermal

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shrinkage ratios of the obtained POFs are shown in Table 4.

As is clear from Table 4, POFs having birefringence absolute values of not larger than 2.0×10^{-4} and excellent heat resistance could be obtained.

Table 4

	Annealing Conditions					Birefringence Absolute Value ($\times 10^{-4}$)	Thermal Shrinkage Ratio (%)	Shrinkage Stress Occurring Temp. (°C)
	Circumferential Velocity of Roller 3 (m/min)	Circumferential Velocity of Roller 4 (m/min)	Roller Circumferential Velocity Ratio	Temp. (°C)	Annealing Time (sec)			
Ex.17	2.5	2.5	1.0	145	60	1.240	0.4	100
Ex.18	5	4.25	0.85	145	32	0.854	0.2	102

1 130 2 06 3 5 4 1 1 3 5 0 2

(Comparative Example 7)

A POF having a fiber diameter of 1,000 μm and a core-sheath structure was obtained in the same manner as in Comparative Example 1 except that the non-contact heating furnace was set to be 135°C and the roller circumferential velocity ratio (circumferential velocity of the roller 2 / circumferential velocity of the roller 1) was set to be 2.5 for drawing. The birefringence and thermal shrinkage ratio of the obtained POF are shown in Table 5.

10 (Examples 19 to 21)

A POF drawn in the same manner as in Comparative Example 7 by use of the first drawing device shown in Fig. 3 was heat treated at annealing temperatures and roller circumferential velocity ratios (circumferential velocity of the roller 4 / circumferential velocity of the roller 3) shown in Table 5 for annealing times shown in Table 5 by use of the annealing device comprising the non-contact heating furnace 6 having a furnace length of 3 m and the rollers 3 and 4, to obtain POFs having a fiber diameter of 1,000 μm and a core-sheath structure. The shrinkage stress occurring temperatures, birefringence absolute values and thermal shrinkage ratios of the obtained POFs are shown in Table 5.

As is clear from Table 5, POFs having birefringence absolute values of not larger than 2.0×10^{-4} , small thermal shrinkage ratios and excellent heat resistance could be obtained.

(Examples 22 and 23)

As is clear from Table 5, POFs having birefringence absolute values of not larger than 2.0×10^{-4} , small thermal shrinkage ratios and excellent heat resistance could be obtained.

As is clear from Table 5, POFs having birefringence absolute values of not larger than 2.0×10^{-4} , small thermal shrinkage ratios and excellent heat resistance could be obtained.

(Comparative Example 8)

A POF having a fiber diameter of 1,000 μm and a core-sheath structure was obtained in the same manner as in Comparative Example 1 except that the non-contact heating furnace 5 was set to be 135°C and the roller circumferential velocity ratio (circumferential velocity of the roller 2 / circumferential velocity of the roller 1) was set to be 2.7 for drawing. The thermal shrinkage ratio of the obtained POF is shown in Table 6.

(Examples 24 to 25)

After wound around a bobbin, a POF drawn in the same manner as in Comparative Example 8 by means of the first drawing device shown in Fig. 3 was heat treated at annealing temperatures and roller circumferential velocity ratios (circumferential velocity of the roller 4 / circumferential velocity of the roller 3) shown in Table 6 for annealing times shown in Table 6 by means of the annealing device comprising the non-contact heating furnace 6 having a furnace length of 3 m and the rollers 3 and 4. The thermal shrinkage ratios of the obtained POFs are shown in Table 6.

Table 6

	Annealing Conditions					Thermal Shrinkage Ratio (%)
	Circumferential Velocity of Roller 3 (m/min)	Circumferential Velocity of Roller 4 (m/min)	Roller Circumferential Velocity Ratio	Temp. (°C)	Annealing Time (sec)	
Comp. Ex. 8	-	-	-	-	-	1.6
Example 24	3.4	3.06	0.9	115	56	0.5
Example 25	3.4	3.06	0.9	110	56	0.4

(Examples 26 to 28)

The same polymers as those used in Example 17 were used in a core, a sheath and a protective layer, and an undrawn POF having a core-sheath-protective-layer structure was prepared by a melt spinning method.

The obtained undrawn POF was drawn by means of the production device 1 shown in Fig. 3 at a temperature of the first non-contact heating furnace 5 of 135°C and a roller circumferential velocity ratio (circumferential velocity of the roller 2 / circumferential velocity of the roller 1) of 2.7 so as to obtain a POF having a birefringence absolute value of 5.912×10^{-4} . This POF was continuously fed into the non-contact heating furnace 6 of the second annealing device of the production device 1 of Fig. 3 and heat treated at a temperature of the non-contact heating furnace 6 having a furnace length of 3 m of 130°C, a roller circumferential velocity ratio (circumferential velocity of the roller 4 / circumferential velocity of the roller 3) of

Further, a POF was drawn under the same conditions as those used in Example 26 by means of the first drawing device of the production device 1 shown in Fig. 3, and the drawn POF was wound around a bobbin. This POF was heat treated by means of the second annealing device of the production device 1 shown in Fig. 3 at a temperature of the non-contact heating furnace 6 having a furnace length of 3 m of 125°C, a roller circumferential velocity ratio (circumferential velocity of the roller 4 / circumferential velocity of the roller 3) of 0.7 and a circumferential velocity of the roller 3 of 3.5 m/min to obtain a POF having a core-sheath-protective-layer structure (Example 27).

Further, a POF was drawn under heating by means of the production device 1 shown in Fig. 3 at a temperature of the first non-contact heating furnace 5 of 140°C and a roller circumferential velocity ratio of 3.3 and then wound around a bobbin. A POF having a birefringence absolute value of 5.833×10^{-4} was obtained. The obtained POF was heat treated at an annealing temperature of the non-contact heating furnace 6 having a furnace length of 3 m in the second annealing device shown in Fig. 3 of 115°C, a roller circumferential velocity ratio (circumferential velocity of the roller 4/circumferential velocity of the roller 3) of

0.9 and a circumferential velocity of the roller 3 of 3.5 m/min to obtain a core-sheath-protective-layer structure (Example 28).

TMA and measurements of birefringences and thermal shrinkage ratios were conducted on these POFs, and a molten polyethylene was continuously applied to the peripheries of these POFs by use of a cable production device to produce POF cables, and the numbers of repeated bending of these POF cables were counted. The results are shown in Table 7. These POFs were excellent in mechanical properties and heat shrinkability because they had birefringence absolute values of not smaller than 1.5×10^{-4} and shrinkage stress occurring temperatures of not lower than $(T_g - 20)^\circ\text{C}$.

Table 7

	Shrinkage Stress Occurring Temp. ($^\circ\text{C}$)	Birefringence Absolute Value	Thermal Shrinkage Ratio (%)	Number of Repeated Bending (times)
Example 26	98	2.157×10^{-4}	0.46	12350
Example 27	100	1.880×10^{-4}	0.37	10240
Example 28	99	3.270×10^{-4}	0.47	18310

(Examples 29 to 30)

The same polymers as those used in Example 17 were used in a core, a sheath and a protective layer, and an undrawn POF having a core-sheath-protective-layer structure was prepared by a melt spinning method.

The obtained undrawn POF was drawn under heating by means of the production device 2 shown in Fig. 5 at a temperature of the first non-contact heating furnace 17 of 140°C and a roller circumferential velocity ratio (circumferential velocity of the roller 15 / circumferential velocity of the roller 14) of 2.7 to obtain a POF having a birefringence absolute value of 4.36×10^{-4} . Except that this POF was continuously fed into the second annealing device shown in Fig. 5 and heat treated at a temperature of the non-contact heating furnace 18 having a furnace length of 2 m of 130°C, a hot air velocity of 7 m/sec, a roller circumferential velocity ratio (circumferential velocity of the roller 16/circumferential velocity of the roller 15) of 0.83 and a circumferential velocity of the roller 15 of 6.8 m/min, a POF having a core-sheath-protective-layer structure was obtained in the same manner as in Example 17 (Example 29).

Further, except that a POF drawn in the same manner as in Example 29 by use of the first production device shown in Fig. 5 was wound around a bobbin and then drew under heating by means of the second annealing device shown in Fig. 5 comprising the non-contact heating furnace 18 having a furnace length of 2.5 m and the rollers 15 and 19 at an annealing temperature of 115°C, a hot air velocity of 7 m/sec, a roller circumferential velocity ratio (circumferential velocity of the roller 16 / circumferential velocity of the roller 15) of 0.95 and a

circumferential velocity of the roller 15 of 2.0 m/min, a POF having a core-sheath-protective-layer structure was obtained in the same manner as in Example 17 (Example 30).

TMA and measurements of birefringences and thermal shrinkage ratios were conducted on these POFs, and molten Nylon 12 was continuously applied to the peripheries of these POFs to form two layers of Nylon 12 on the POFs by use of a cable production device so as to produce POF cables, and the numbers of repeated bending of these POF cables were counted. The results of these measurements and tensions at the time of annealing are shown in Table 8. These POFs were excellent in mechanical properties and heat shrinkability because they had birefringence absolute values of not smaller than 1.5×10^{-4} and shrinkage stress occurring temperatures of not lower than $(T_g - 20)^\circ\text{C}$.

Table 8

	Tension (Pa)	Shrinkage Stress Occurring Temp. ($^\circ\text{C}$)	Birefringence Absolute Value	Thermal Shrinkage Ratio (%)	Number of Repeated Bending (times)
Example 29	1.47×10^6	99	2.03×10^{-4}	0.45	27150
Example 30	1.31×10^6	99	2.78×10^{-4}	0.41	49320

(Comparative Example 9)

The same polymers as those used in Comparative Example 1 were used in a core and a sheath.

These polymers were fed into a multi-component fiber spinning nozzle heated at 230°C, and an undrawn POF was prepared by a melt spinning method. The obtained undrawn POF was drawn by use of a drawing device comprising the rollers 21 and 22 and non-contact heating furnace 23 shown in Fig. 6. The drawing was carried out at a furnace length of the non-contact heating furnace of 3 m, a hot air velocity of 6 m/sec, a hot air temperature (annealing temperature) of 135°C and a roller circumferential velocity ratio (circumferential velocity of the roller 22 / circumferential velocity of the roller 21) of 2.7. A POF having a diameter of 1,000 μm and a core-sheath structure was obtained. The T_g of the core of the POF was 112°C (DSC method, temperature rising rate: 10°C/min). The thermal shrinkage ratio of the obtained POF is shown in Table 9. (Comparative Example 10)

A POF having a diameter of 1,000 μm and a core-sheath structure was obtained in the same manner as in Comparative Example 9 except that the velocity of hot air at the time of drawing was changed to 9 m/sec. The thermal shrinkage ratio of the obtained POF is shown in Table 9. (Example 31)

After wound around a bobbin, the POF obtained in Comparative Example 9 was then heat treated by use of the production device 4 shown in Fig. 7 which had a furnace length of 2 m. The annealing was conducted at a hot air velocity of 6 m/sec, a circumferential velocity of the

(Example 32)

Polymethyl methacrylate obtained by continuous bulk polymerization was used as a core. A copolymer of 51 parts by weight of 2,2,2-trifluoromethyl methacrylate, 30 parts by weight of 1,1,2,2-tetrahydroperfluorodecyl

These polymers were fed into a multi-component fiber spinning nozzle heated at 230°C, and an undrawn POF was prepared by a melt spinning method. The obtained undrawn POF was drawn by use of the production device 3 comprising the rollers 21 and 22 and non-contact heating furnace 3 shown in Fig. 6. The drawing was carried out at a furnace length of the non-contact heating furnace of 2.5 m, a hot air velocity of 6 m/sec, a hot air temperature (annealing temperature) of 140°C and a roller circumferential velocity ratio (circumferential velocity of the roller 22 / circumferential velocity of the roller 21) of 2.7. A POF having a diameter of 1,000 μm and a core-sheath-protective-layer structure was obtained. The Tg of the core of the POF was 112°C (DSC method, temperature rising rate: 10°C/min). The thermal shrinkage ratio of the obtained POF is shown in Table 9.

As shown in Fig. 8, a stainless steel porous plate 33 having a plurality of pores each having a diameter of 0.5 mm all over its surface and a wedge-shaped path for passing a POF on the surface was disposed in the production device 3 having a furnace length of 2 m shown in Fig. 6 in the manner shown in Fig. 9 to prepare an annealing device.

Arrows in Figs. 8 and 9 indicate directions of hot air. Further, Fig. 8(a) is a plan view of the porous plate 33 with a POF 24 placed in the wedge-shaped path, Fig. 8(b) is a cross sectional view of the POF of Fig. 8(a) in the longitudinal direction, and Fig. 8(c) is a cross sectional view of the POF of Fig. 8(a) in a direction perpendicular to the longitudinal direction. Using this annealing device, the POF of Comparative Example 11 which had been wound around a bobbin was heat treated at a velocity of hot air from the hot air generator of 6 m/sec, a circumferential velocity of the roller 21 of 2 m/min, and a hot air temperature and roller circumferential velocity ratio (circumferential velocity of the roller 22 / circumferential velocity of the roller 21) shown in Table 9. Tensions at the time of the annealing, thermal shrinkage ratios, shrinkage stress occurring temperatures and birefringence absolute values before and after the annealing of the obtained POF are shown in Tables 9 and 10.

Table 9

	Annealing Conditions		Tension at Annealing (Pa)	Thermal Shrinkage Ratio (%)
	Temp. (°C)	Circumferential Velocity Ratio		
Comp.Ex.9	-	-	-	2.2
Comp.Ex.10	-	-	-	1.6
Example 31	115	0.9	0.43×10^6	0.4
Example 32	110	0.9	1.2×10^6	0.4
Comp.Ex.11	-	-	-	1.3
Example 33	115	0.93	0.81×10^6	0.3

Table 10

	Birefringence Absolute Value		Shrinkage Stress Occurring Temp. (°C)
	before Annealing	after Annealing	
Example 31	5.88×10^{-4}	2.31×10^{-4}	99
Example 32	4.33×10^{-4}	2.45×10^{-4}	99
Example 33	4.35×10^{-4}	2.33×10^{-4}	101

CLAIMES

1. A plastic optical fiber having a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than [(a glass transition temperature of a core) - 35]°C.

2. The plastic optical fiber as claimed in claim 1, wherein the core comprises a homopolymer of methyl methacrylate, or a copolymer comprising a methyl methacrylate unit and another monomer unit.

3. The plastic optical fiber as claimed in claim 1, wherein the core comprises a homopolymer of methyl methacrylate and has a birefringence absolute value of not larger than 2.0×10^{-4} .

4. A plastic optical fiber which has a core comprising a homopolymer of methyl methacrylate and having a birefringence absolute value of not smaller than 1.5×10^{-4} and has a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than [(a glass transition temperature of the core) - 20]°C.

5. The plastic optical fiber as claimed in any one of claims 1 to 4, which exhibits a shrinkage ratio of not higher than 2% when heated at 90°C for 65 hours.

6. The plastic optical fiber as claimed in claim 4, which exhibits a shrinkage ratio of not higher than 0.5% when heated at 90°C for 65 hours.

5

7. A plastic optical fiber cable obtained by forming a coating layer around the plastic optical fiber as claimed in any one of claims 1 to 6.

10

8. A plastic optical fiber cable that has a protective layer comprising a vinylidene fluoride-tetrafluoroethylene copolymer formed around the plastic optical fiber as claimed in any one of claims 1 to 6 having a core-sheath structure in which the sheath comprises a polymer containing a fluorine-based methacrylate unit or a vinylidene fluoride unit and that has a coating layer comprising Nylon 12 formed on the protective layer.

15

9. A plugged plastic optical fiber cable obtained by attaching a plug on the tip of the plastic optical fiber cable as claimed in claim 7 or 8.

20

10. A production method of a plastic optical fiber, comprising the steps of heat-drawing an undrawn plastic optical fiber obtained by melt spinning and annealing the drawn fiber at a circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear

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14. A production method of a plastic optical fiber, comprising the step of annealing a plastic optical fiber obtained by the method as claimed in any one of claims 10 to 13 at a temperature not higher than [(a glass transition
5 temperature of a core) + 8]°C.

15. A plastic optical fiber obtained by the method as claimed in any one of claims 10 to 14 and having a shrinkage stress occurring temperature obtained by
10 thermomechanical analysis of not lower than [(a glass transition temperature of a core) - 35]°C.

16. The plastic optical fiber as claimed in claim 15, wherein the core comprises a homopolymer of methyl
15 methacrylate and has a birefringence absolute value of not larger than 2.0×10^{-4} .

17. A plastic optical fiber obtained by the method as claimed in any one of claims 10 to 14, having a core
20 which comprises a homopolymer of methyl methacrylate and has a birefringence absolute value of not smaller than 1.5×10^{-4} , and having a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than [(a glass transition temperature of the core) - 20]°C.

25

18. The plastic optical fiber as claimed in claim 15, 16 or 17, which exhibits a shrinkage ratio of not higher

than 2% when heated at 90°C for 65 hours.

19. A plastic optical fiber cable obtained by forming a coating layer around the plastic optical fiber as
5 claimed in any one of claims 15 to 18.

20. A plugged plastic optical fiber cable obtained by attaching a plug on the tip of the plastic optical fiber cable as claimed in claim 19.

10

21. A production method of a plastic optical fiber, comprising the steps of heat-drawing an undrawn plastic optical fiber obtained by melt spinning and annealing the drawn fiber at a circumferential velocity ratio
15 (circumferential velocity of a rear roller/circumferential velocity of a front roller) between the front and rear rollers of 0.5 to 1.2 under heating conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$ [T_{gc}: a glass transition temperature of a core, x: an
20 annealing temperature (°C), and y: annealing time (seconds)] while a tension of 0.35×10^6 to 1.5×10^6 Pa is applied to the fiber.

22. A production method of a plastic optical fiber,
25 comprising the step of annealing a plastic optical fiber obtained by melt spinning, at a temperature from (a glass transition temperature of a core - 5)°C to (the glass

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transition temperature of the core + 80)°C while a tension of 0.35×10^6 to 1.5×10^6 Pa is applied to the fiber.

23. The production method as claimed in claim 22,
5 which has the step of heat-drawing a plastic optical fiber and carrying out the annealing after heat-drawing the plastic optical fiber.

24. The production method as claimed in claim 21,
10 22 or 23, wherein a polymer containing a methyl methacrylate unit in an amount of not smaller than 70% by weight is used as the core of a plastic optical fiber.

25. The production method as claimed in claim 22 or
15 23, wherein a homopolymer of methyl methacrylate is used as the core of a plastic optical fiber and the annealing is carried out at a temperature not higher than (a glass transition temperature of the core + 30)°C such that the core has a birefringence absolute value of not smaller than
20 1.5×10^{-4} and the plastic optical fiber has a shrinkage stress occurring temperature obtained by thermomechanical analysis of not lower than [(the glass transition temperature of the core) - 20]°C.

25 26. The production method as claimed in any one of claims 21 to 25, wherein the annealing is carried out by introducing a plastic optical fiber into an annealing zone

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fiber.

32. A production method of a plugged plastic
optical fiber cable, comprising the steps of obtaining a
5 plastic optical fiber cable by the method as claimed in
claim 31, and then attaching a plug on the tip of the
obtained optical fiber cable.

ABSTRACT

The present invention relates to a production method of a plastic optical fiber which comprises the steps of heat
 5 drawing an undrawn plastic optical fiber obtained by melt spinning and annealing the drawn fiber at a circumferential velocity ratio between the front and rear rollers (circumferential velocity of a rear roller / circumferential velocity of a front roller) of 0.5 to 1.2 under heating
 10 conditions which satisfy $4 \leq y \leq -1.5x + 330$ and $(T_{gc} - 5)^{\circ}\text{C} \leq x \leq (T_{gc} + 110)^{\circ}\text{C}$ [T_{gc} : a glass transition temperature of a core, x : an annealing temperature ($^{\circ}\text{C}$), and y : an annealing time (seconds)]. According to the present invention, a plastic optical fiber having a small thermal
 15 shrinkage ratio and excellent heat resistance can be provided.

FIG. 1

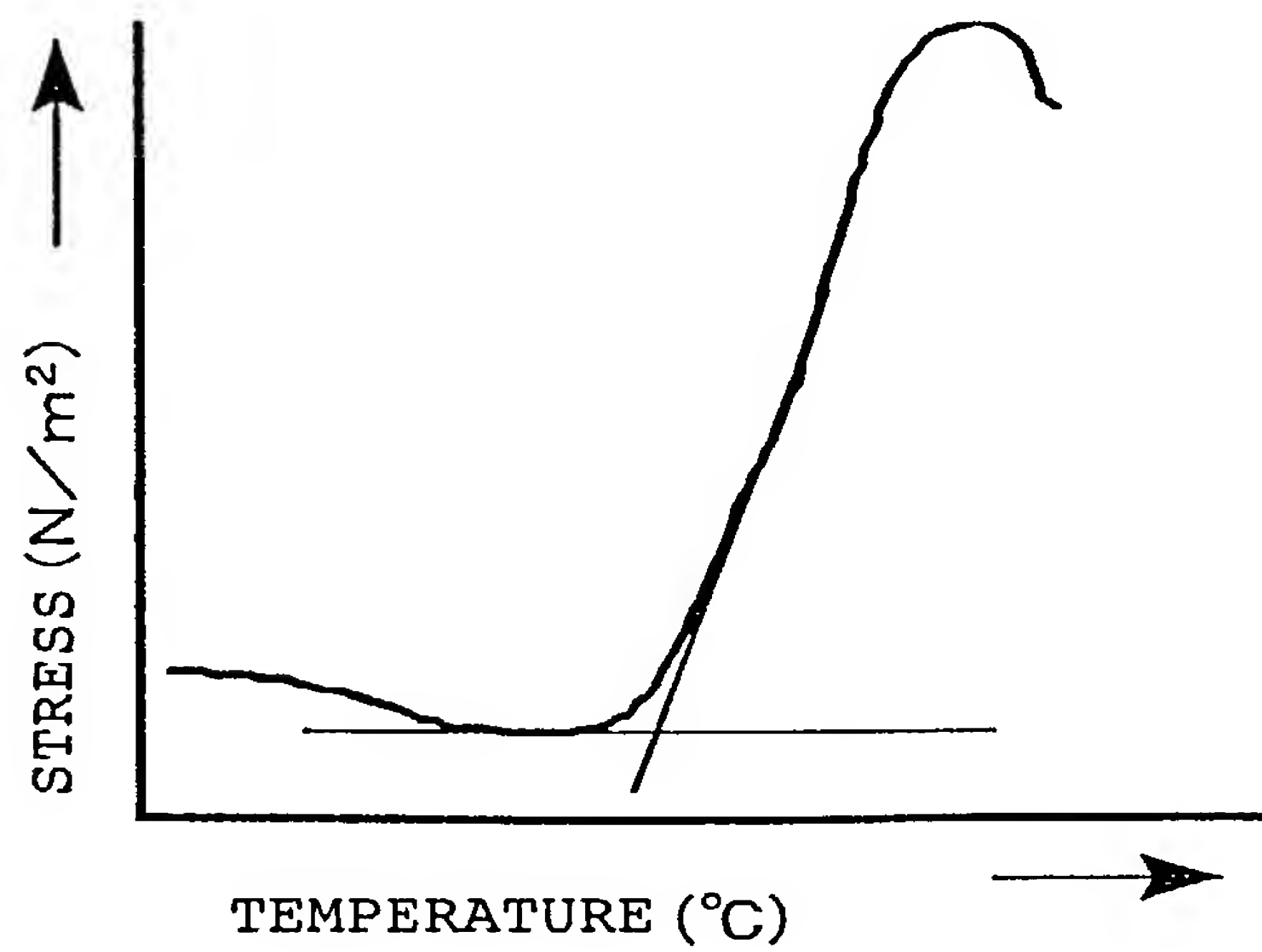


FIG. 2

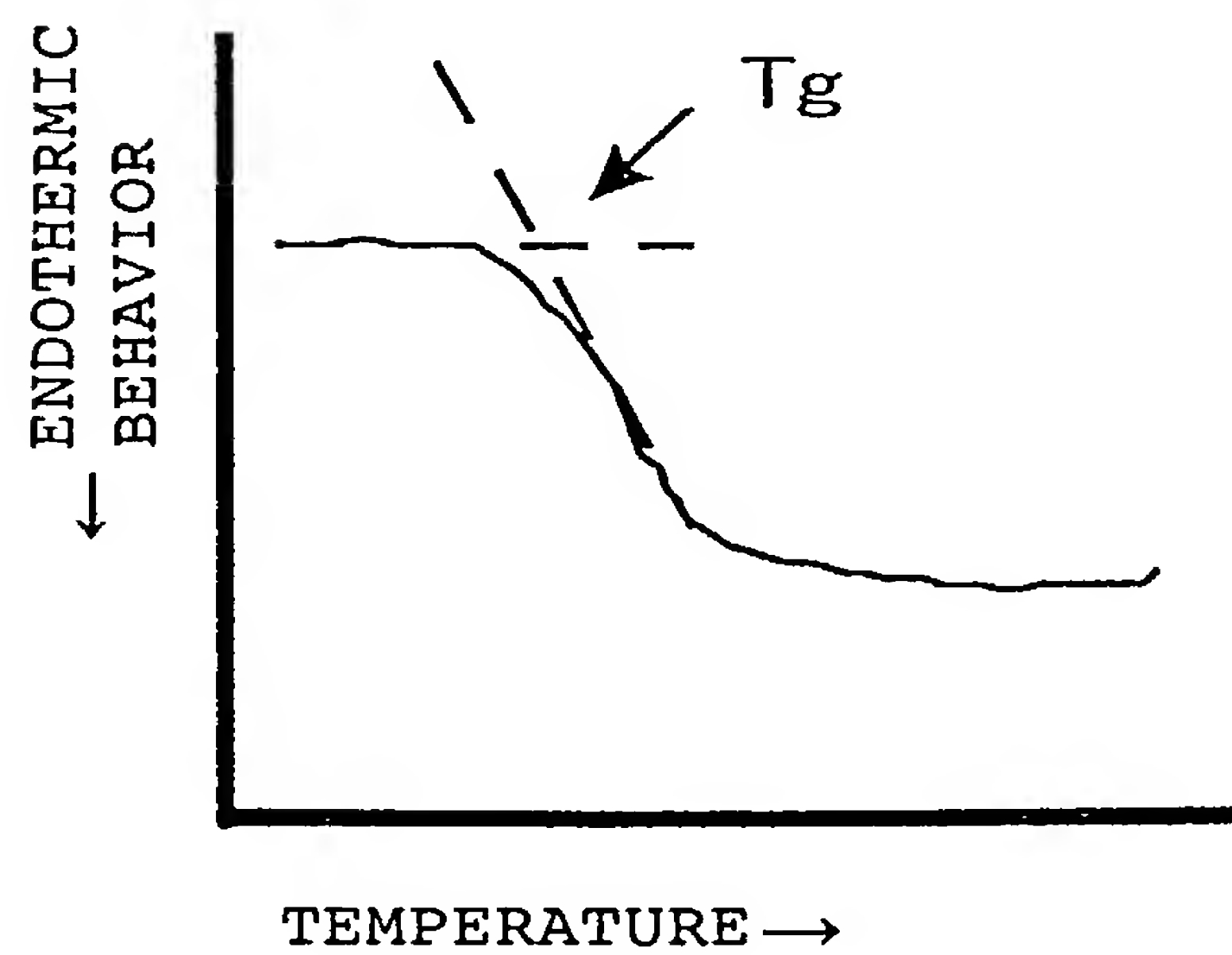
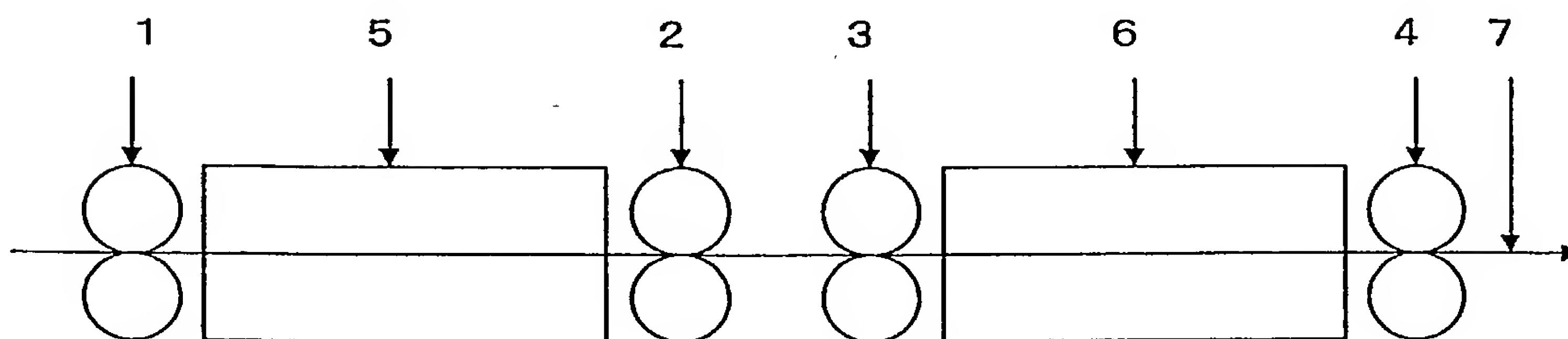


FIG. 3



The diagram illustrates a closed-loop system for a mobile robot. The robot, labeled 10, is shown at the bottom center, moving upwards along a solid line path 11. The path leads to a 180-degree turn around a central point O, which is flanked by two circular obstacles 9. The path then continues as a dashed line 12, leading to a square block 13. The robot is shown at the start of the path, and the path ends at the square block 13.

A schematic diagram of a mechanical assembly. It features a horizontal shaft with several components. From left to right: a pair of stacked circles (14) with a downward arrow; a rectangular block (17) with a downward arrow; another pair of stacked circles (15) with a downward arrow; a second rectangular block (18) with a downward arrow; a third pair of stacked circles (16) with a downward arrow; and a final downward arrow (19) further to the right. A vertical arrow (20) points upwards at the junction between the second rectangular block (18) and the third pair of circles (16).

FIG. 6

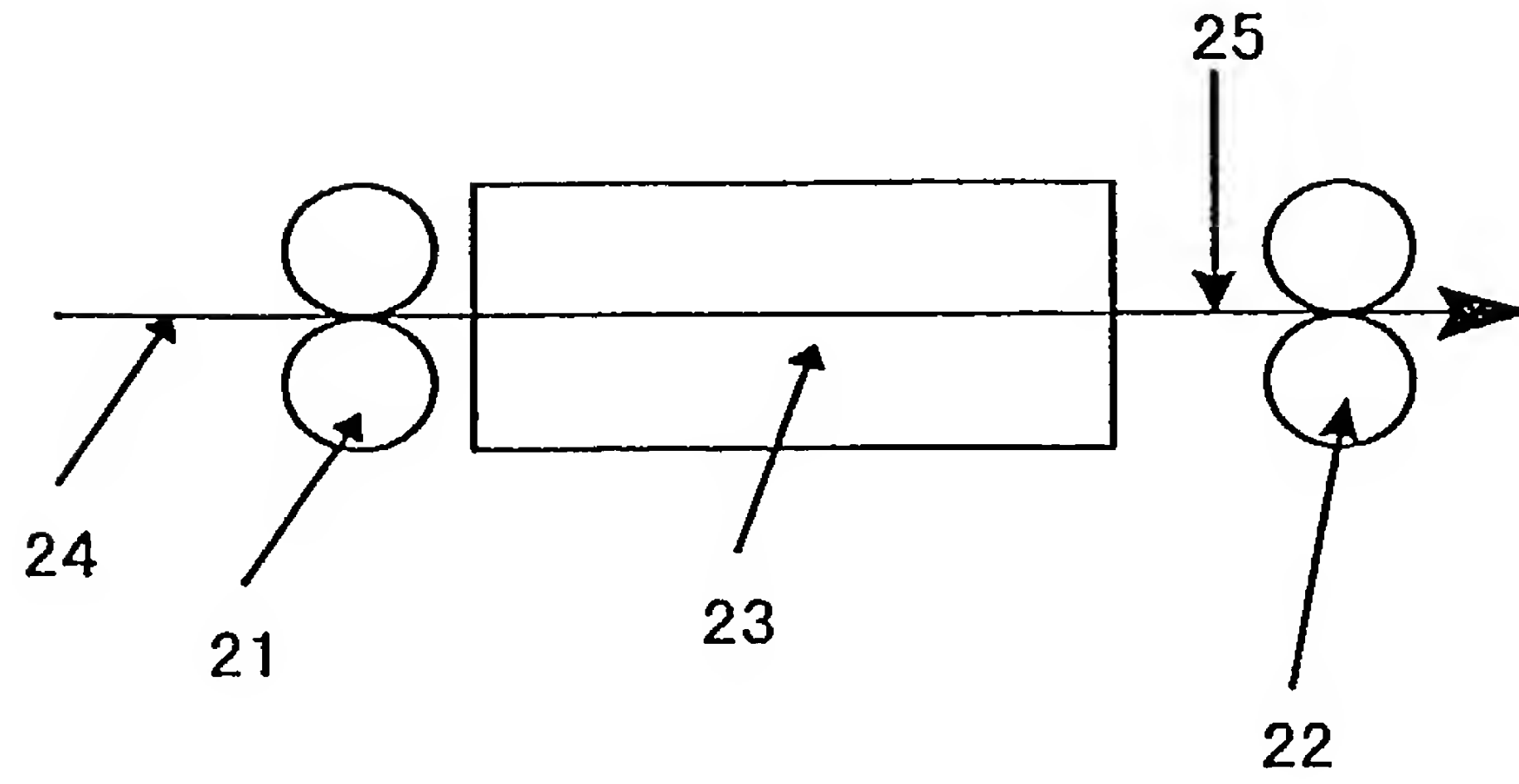
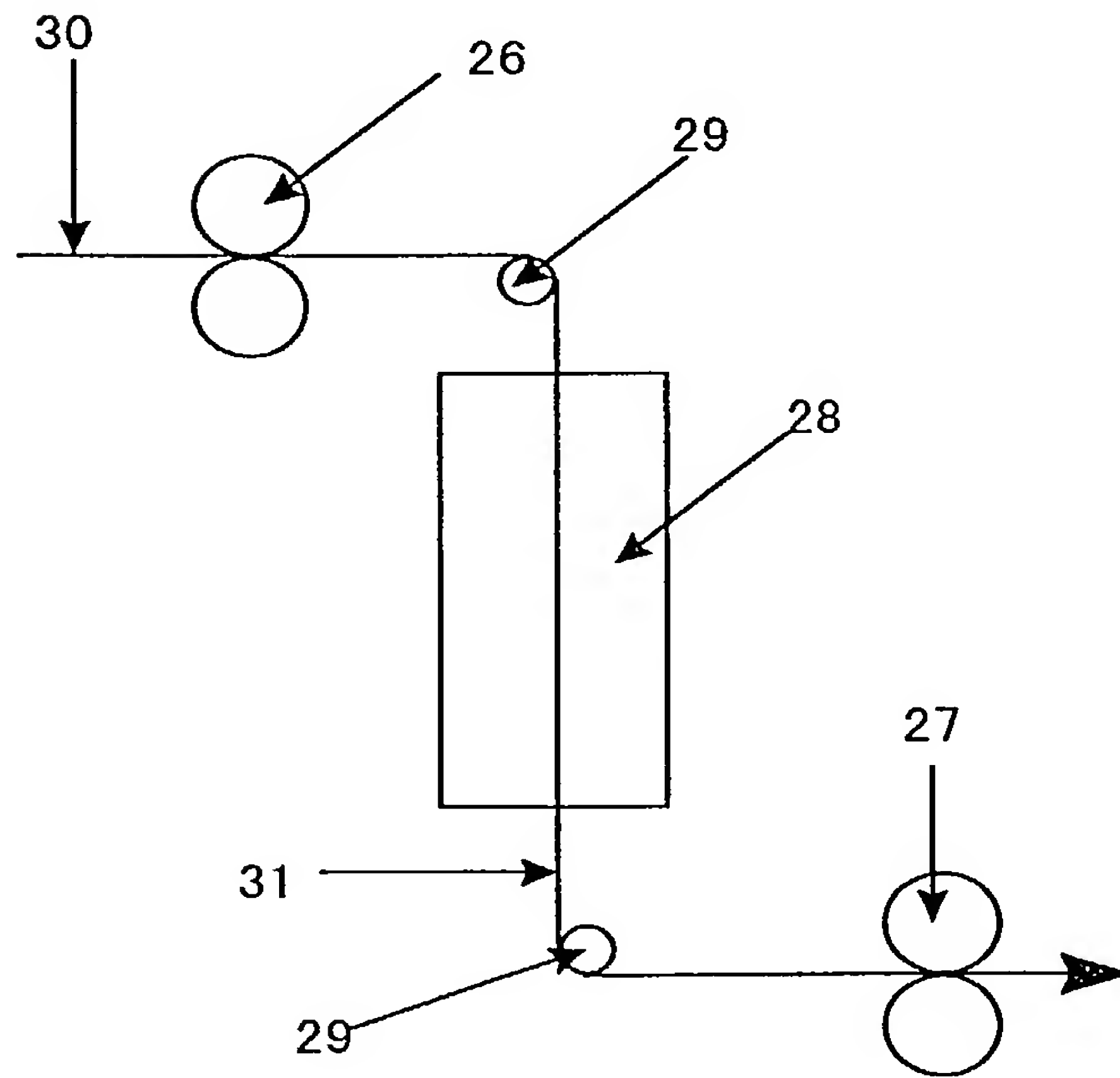


FIG. 7



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FIG. 8

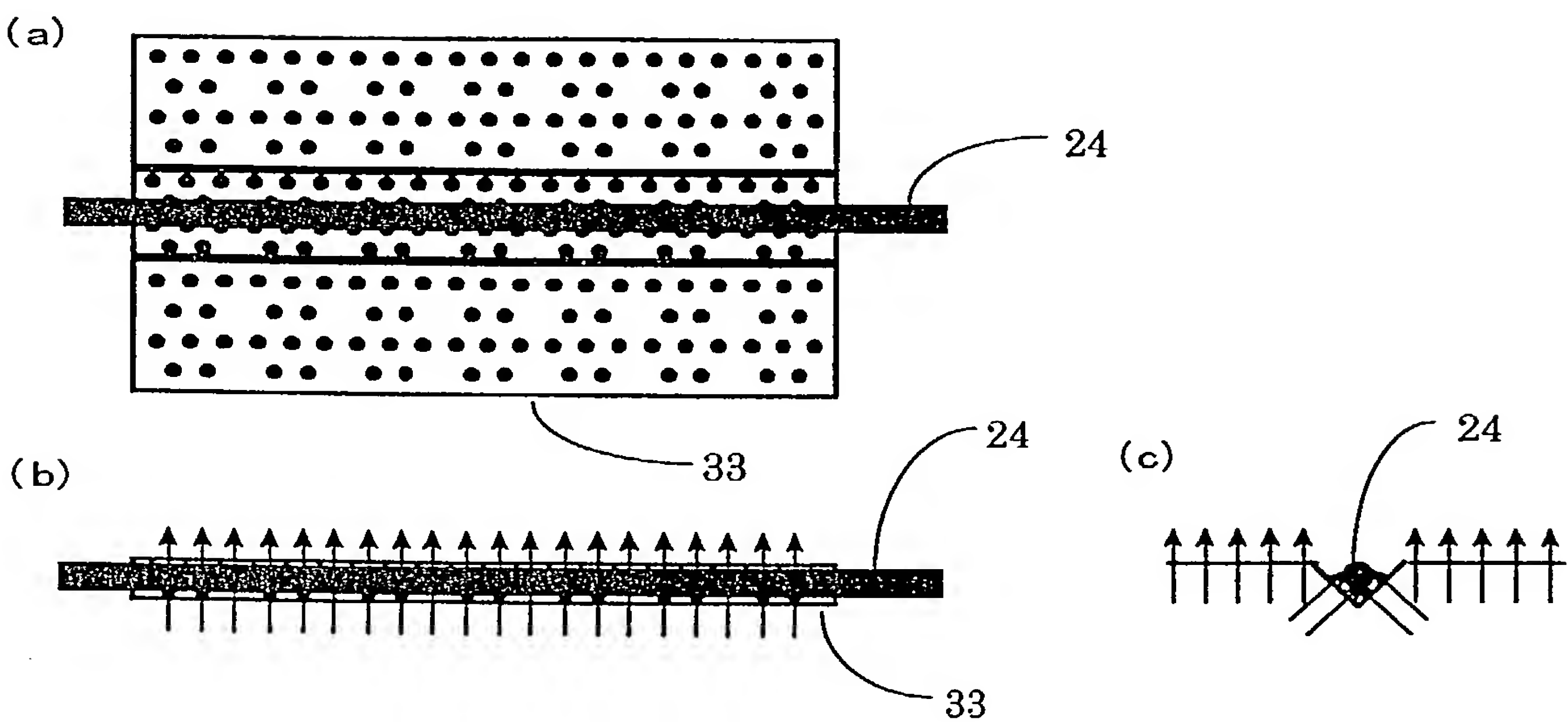
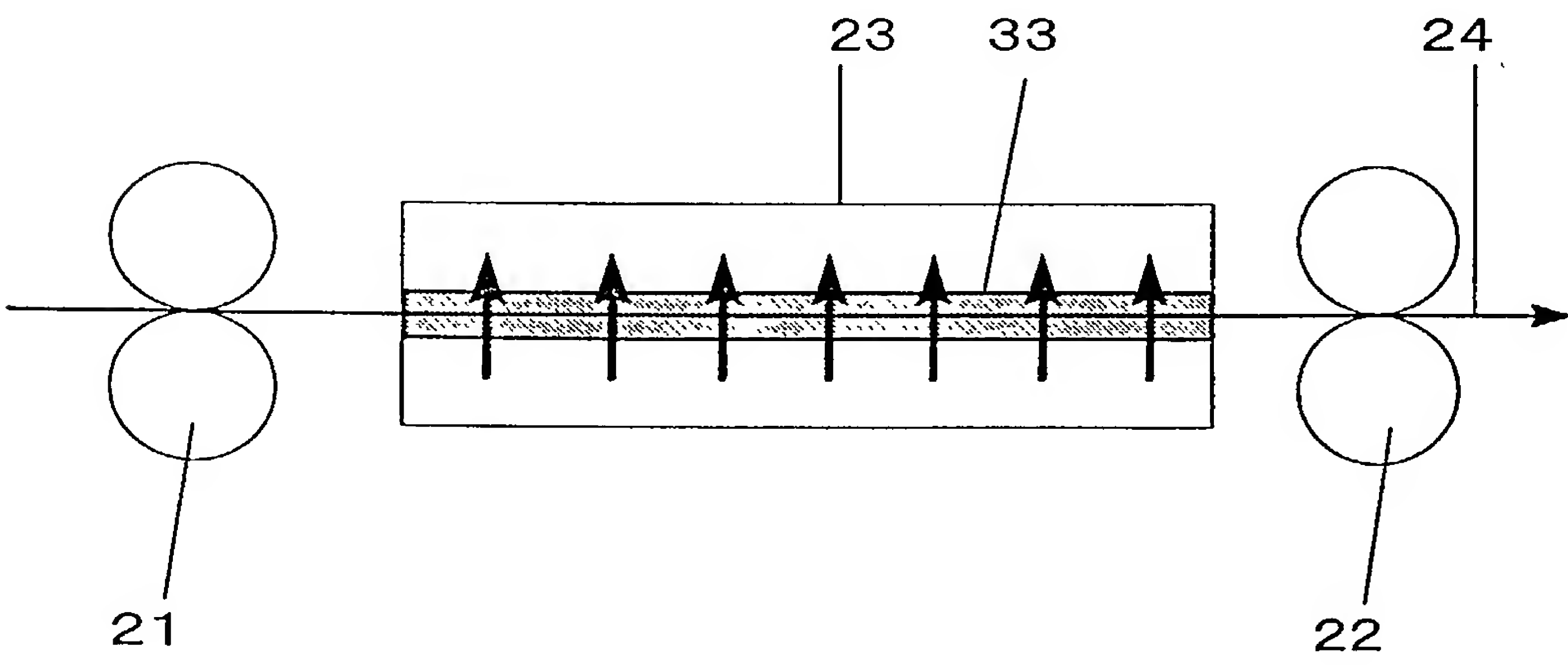


FIG. 9



FOR UTILITY/DESIGN
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ORIGINAL/SUBSTITUTE/SUPPLEMENTAL
DECLARATIONS

RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Plastic Optical Fiber, Optical Fiber Cable, Plugged Optical Fiber Cable, and
Production Methods Thereof

(Title of Invention)

the specification of which (check applicable box(es)):

- A. ☐ is attached hereto.
B. ☒ was filed on March 8, 2002 as U.S. Application No. 10/070,616
C. ☒ was filed as PCT International Application Number PCT/JP00/06093 on September 7, 2000
and (if applicable to U.S. or PCT application) was amended on _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment specifically referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56. I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below, and I have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or any PCT international application, on this invention filed by me or my legal representatives or assigns and having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

Number(s)	Country	Day/MONTH/Year Filed	Date first Laid- open or Published	Date Patented or Granted	Priority NOT Claimed
11-255802	Japan	09/09/1999			
2000-058812	Japan	03/03/2000			
2000-068866	Japan	13/03/2000			

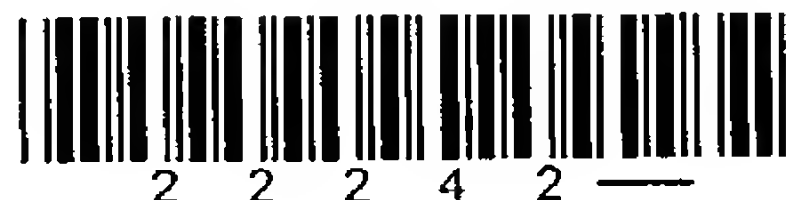
If more prior foreign applications, X box at bottom and continue on attached page.

Except as noted below, I hereby claim domestic priority benefit under 35 U.S.C. 119(e) or 120 and/or 365(c) of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S)

Appln. No. (series code/serial no.)	Day/MONTH/Year Filed	Status pending, abandoned, patented	Priority NOT Claimed

As a named inventor, I hereby appoint the practitioners associated with Customer Number 22242, with full power of substitution and revocation, to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith, and request that all correspondence and telephone calls in respect to this application be directed to FITCH, EVEN, TABIN & FLANNERY, Suite 1600, 120 South LaSalle Street, Chicago, Illinois 60603-3406, Telephone No. (312) 577-7000, Facsimile No. (312) 577-7007, CUSTOMER NUMBER 22242.



2 2 2 4 2

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made herein on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity or enforceability of the application or any patent issued thereon.

☐ Additional inventors, see attached pages.

☐ Additional foreign prior art on attached page (incorporated herein by reference)

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